Thermodynamics of irreversible processes – past and present

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Tensor notation

Throughout this report we use index notation for vectors and tensors. Summation over repeated indices is understood so that, for instance, $\frac{\partial v_l}{\partial x_l}$ denotes the divergence of the velocity v, and $q_i n_i$ is the component of the heat flux q in the direction of the unit vector n.

Indices enclosed by round brackets indicate symmetrisation so that

$$a_{(i_1 i_2 \dots i_n)} = \frac{1}{n!} P\left(a_{i_1 i_2 \dots i_n}\right),$$

where P is the permutation operator. In particular we have

$$\frac{\partial v_{(i}}{\partial x_{j)}} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right).$$

Triangular and square brackets represent symmetric, traceless tensors and antisymmetric tensors respectively, for instance

$$\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) - \frac{1}{3}\frac{\partial v_l}{\partial x_l}\delta_{ij}, \qquad \text{and}$$

$$\frac{\partial v_{[i}}{\partial x_{j]}} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right).$$

Preview

Irreversibility is the phenomenon that makes a thermodynamic body tend to equilibrium, a state of stationary and homogeneous fields of chemical potentials, velocity, and temperature, albeit in lively fluctuating *thermal* molecular motion, unnoticed by the naked eye. The random character of the fluctuations is maintained by contact with the boundary. 19th century physics assumed equal probability for all manifestations

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of the thermal motion and succeeded to relate irreversibility to entropy, a quantity with a strong probability – albeit no certainty – of growth. Thus irreversibility was identified as a probabilistic phenomenon in which bodies progress from fields of low probability to fields of high probability. Such is the meaning of irreversibility in natural philosophy. We explain this in some detail in Section 2 and show that an isolated body has no real irreversibility.

In a more practical sense irreversible, or *dissipative* phenomena like diffusion, friction and heat conduction – created by gradients of chemical potentials, velocity and temperature, respectively, – were successfully described by *parabolic* differential equations, read off from observations: the laws of Fick, Navier-Stokes, and Fourier. These laws serve engineers well and will continue to do so in the future. The laws were formulated in the 19th century and later – in the 20th century – they were incorporated into Eckart's theory, usually dubbed TIP, for thermodynamics of irreversible processes. This theory is described in Section 4. It might also be called the doctrine of forces and fluxes, because it provides linear relations between *thermodynamic forces*, like the gradients of velocity and temperature, and *thermodynamic fluxes*, like the deviatoric stress and the heat flux.

An interesting feature of the theory lies in the possibility of cross effects between heat conduction and diffusion, a phenomenon which does indeed occur. Thus a heat flux may be created by a gradient of chemical potentials, or a diffusion flux may be influenced by a temperature gradient. Such cross effects are also allowed between chemical reaction rates and dynamical pressure. For instance, a chemical affinity may affect the non-equilibrium pressure. The cross effects are limited by the linear representation theory of tensorial functions of tensors of different ranks, a limitation which in the parlance of TIP is given the status of a principle called the Curie principle.

Eckart's theory is highly successful in fluid mechanics, gas dynamics and thermodynamics. It can cope analytically with calm or smooth irreversible processes. However it is true that there used to be cases, before the advent of the computer and of finite element methods, in which the equations could not be solved, such as the sudden expansion of a gas into a low-pressure chamber, where turbulent motion and highly non-homogeneous temperature fields occur. Nowadays even such precipitous irreversible processes may be followed in detail and with good results by numerical methods applied to Eckart's theory, albeit with considerable effort. In earlier times this was impossible. And yet, even then, even without numerical means, for some cases the eventual equilibrium after a sudden irreversible expansion or compression could be predicted. In other precipitous cases, indeed in most of them, nothing could be done. Section 1.4 gives examples.

TIP does not stop at transport phenomena like heat conduction, viscous friction and diffusion. It incorporates chemical reactions into the linear force-flux scheme by setting reaction rates proportional to chemical affinities. The affinities are combinations of chemical potentials of the constituents of a mixture and those in turn are often strongly non-linear functions of the concentrations. Thus Eckart's theory – a *linear* theory of irreversible thermodynamics, valid close to chemical equilibrium – gives rise to non-linear differential equations for the concentrations. And those equations exhibit all the rich mathematical properties of non-linear ordinary and partial differential equations like limit cycles, pattern formation, and – sometimes – chaos.

However, the laws of Fick, Fourier, and Navier-Stokes have one common drawback: they lead to parabolic field equations, which means that they predict infinite speeds of propagation of disturbances in chemical potentials, temperature and shear stress. Engineers do not care, but the phenomenon is anathema for physicists; they called it a paradox, e.g. the *paradox of heat conduction*. Physicists prefer hyperbolic equations which account properly for inertia, stability, and finite speeds of propagation. And yet, for more than a century the flaw of infinite speeds in the classical theories was

passed over in scientific papers and textbooks – with some glib remark or other – until a resolution was proposed. That might have happened for diffusion, or viscous friction but, as it was, it happened for heat conduction at the hands of Cattaneo, a mathematical physicist. Thus a reformulation of Fourier's law became the pivotal point in the transition of thermodynamics from parabolicity to hyperbolicity. Let us consider Cattaneo's argument right here among these introductory remarks, so as to be able to refer back to it on the numerous occasions when the subject of finite speeds and stability arises. Most often – but not always – that happens in rarefied gases where steep gradients can occur in the thermodynamic fields, or rapid rates of change.

Cattaneo argued that in a gas the heat flux q_i at some time t should not only depend on the gradient of temperature $\frac{\partial T}{\partial x_i}$ at that time – as Fourier had had it – but on the *history* of that gradient. This implies a functional relation between $q_i(t)$ and the history $\frac{\partial T}{\partial x_i}(t - \tau)$ of $\frac{\partial T}{\partial x_i}$, where $t - \tau$ is some time in the past, so that τ must be positive. Cattaneo further assumed that the gas has fading memory so that, perhaps, the remembered part of the history can be represented by a short Taylor expansion of $\frac{\partial T}{\partial x_i}(t - \tau)$ into the past at the *present* time, viz.

$$\frac{\partial T}{\partial x_i}(t - \tau) \approx \frac{\partial T}{\partial x_i}(t) - \tau \frac{\partial^2 T}{\partial t \partial x_i}(t).$$

Thus the modified form of Fourier's law would read[1]

$$q_i = -\kappa \left(1 - \tau \frac{\partial}{\partial t}\right) \frac{\partial T}{\partial x_i} \qquad \text{or equivalently} \qquad \frac{1}{1 - \tau \frac{\partial}{\partial t}} q_i = -\kappa \frac{\partial T}{\partial x_i}. \qquad (P.1)$$

If that equation is used to eliminate the heat flux from the energy equation of a body at rest we obtain the equation[2]

$$\rho c \frac{\partial T}{\partial t} = \kappa \left(\frac{\partial^2 T}{\partial x_i \partial x_i} - \tau \frac{\partial^3 T}{\partial t \partial x_i \partial x_i}\right). \qquad (P.2)$$

Now, ironically, that equation is still parabolic, and it still predicts infinite speed of propagation. Thus Cattaneo's argument defeated his purpose. However, a good physicist does not let himself be bogged down by mere mathematics. Thus the physicist in Cattaneo got the better of the mathematician and he wrote

$$\frac{1}{1 - \tau \frac{\partial}{\partial t}} \approx 1 + \tau \frac{\partial}{\partial t}$$

on the basis that τ is small. Thus equation $(P.1)_2$ becomes

$$\underline{\underline{q_i}} + \tau \frac{\partial q_i}{\partial t} = \underline{-\kappa \frac{\partial T}{\partial x_i}}. \qquad (P.3)$$

This is the Cattaneo equation which extends the Fourier law, the underlined part of the equation. Cattaneo's equation created some attention, because elimination of q_i between it and the energy equation provides a hyperbolic equation, namely the telegraph equation equation, the prototype of all hyperbolic differential equations of second order.

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \frac{\kappa}{\rho c} \frac{\partial^2 T}{\partial x_i \partial x_i}. \qquad (P.4)$$

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[1] κ is the thermal conductivity.

[2] ρ is the mass density and c is the specific heat at constant volume.

That equation implies a finite speed of propagation, which is what Cattaneo wanted, and what physicists at large want.

Now, finite speeds are largely equivalent to stability. Let us consider this in a rough-and-ready but still potent manner – at the Cattaneo level of reasoning.

Equation (P.1) implies that, if the heat flux is zero at some point, the temperature gradient grows to infinity which is obviously nonsense. On the other hand, equation (P.3) implies that, if the temperature gradient vanishes at some point, the heat flux relaxes to zero at that point, which makes sense. Therefore the Cattaneo equation (P.3) is superior to equation (P.1) as regards to stability as well as finite speeds. Consequently *we must reject the idea to approximate the history of the temperature gradient by a short Taylor series* despite its inherent plausibility.

The paradox of heat conduction is not alone; it is the tip of an iceberg. There are analogous paradoxes for viscous friction and diffusion in gases. In addition the grade theories of visco-elastic fluids exhibit a very similar paradox when the history of deformation is replaced by a Taylor series with Rivlin-Ericksen tensors as expansion coefficients. In the kinetic theory of gases the approximation schemes of Maxwell and Enskog are similarly flawed; they ought to be discarded.

All of this is explained in the appropriate places in this report. Section 5 deals with rational thermodynamics, a theory which was effectively brought down by its failure to produce stable solutions in visco-elasticity. Section 6 considers mixtures. Actually mixtures represent a special case: they do not need a Cattaneo-type argument for the improvement of Fick's law. Indeed, as soon as Fick's law is recognised as a mutilated form of the equations of balance of momenta, a physicist will easily improve the theory by taking account of the inertia of the diffusive motion of the constituents. This is equivalent to Cattaneo's reasoning but more plausible and, indeed, physically nearly trivial.

Extended thermodynamics offers a way out of the dilemma represented by infinite speeds and failing stability. Extended thermodynamics *of gases* has profited much from the knowledge of the kinetic theory of gases. Therefore a chapter has been included in this report about Boltzmann's kinetic theory which in itself, and in conjunction with Grad's iterative scheme, avoids all paradoxes, or at least those that occur in gases.

After that, Sections 8 and 9 give an account of extended thermodynamics. Section 8.2 describes the heuristic beginnings, Section 8.3 exhibits the close relationship between the theory and the kinetic theory of gases, and Section 8.4 represents the culmination of extended thermodynamics: the emergence of symmetric hyperbolic field equations – to replace the old parabolic equations – at the dictate of a fully general entropy principle. Section 9 applies extended thermodynamics to light scattering. It provides the ultimate proof of the applicability and practicality of the theory.

Irreversible thermodynamics has not entirely escaped the attention of the Swedish Nobel committee. Onsager was honoured in 1968, and Prigogine in 1977, both for chemistry. The work of both was never quite undisputed, particularly not *before* the prizes were awarded.

Onsager's work is discussed in Section 3. Its decisive assumption concerns thermal molecular fluctuations. Onsager states that, *in the mean*, these fluctuations behave like macroscopic fields in relaxation toward equilibrium. That hypothesis – along with the whole thesis – was rejected by the doctoral committee in Onsager's home university, and it was never proven to this day; the hypothesis is most unlikely to be true and the best one can say about it is that *it is not altogether unreasonable*. This faint praise was issued by de Groot and Mazur, the authors of the most influential monograph on irreversible thermodynamics. And yet! And yet, light scattering spectra could not be successfully evaluated – as they are – unless Onsager's mean-regression hypothesis

were true. So we may say – reluctantly – that the hypothesis is a stroke of genius, unproven but true, perhaps.

With Prigogine it is different. His main pronouncement is the principle of minimal entropy production. That principle states that under given boundary condition, a body will tend to a state, in the eventual stationary process, that has a minimum of entropy production. The assertion can be disproved in two lines, see Section 4.2.4. Apart from that, however, Prigogine deserves recognition, because among chemists he popularised the rich mathematical properties of the solutions of non-linear differential equations in coupled chemical reactions. In addition, he invented the Brusselator in order to illustrate that cyclic chemical processes can occur in a homogeneous body under a constant in- and efflux of chemical constituents.

It is often the case in thermodynamics that a complex mathematical argument is required to express a simple physical idea. On such occasions, in this report, we shall consistently prefer plausibility over rigour and present the easy suggestive argument rather than the mathematically sophisticated one. This is done in order to accommodate the non-expert reader. Unfortunately such simplification is not always possible, it is most often impossible for non-linear phenomena in irreversible thermodynamics, notably for the results of Boltzmann's formal kinetic theory of gases. Therefore we must urgently recommend that researchers – physicists and historians – apply themselves to a profound study of molecular theories. We dare say that successful research in non-linear irreversible thermodynamics is impossible without that background.

Finally, a remark in our own cause: we, the authors of this report, have been blamed by the reviewers of a previous draught, that we give too much weight to our personal opinions about the development of irreversible thermodynamics. That reproof is misplaced! We present nothing else but demonstrable historical facts, and back them up with the appropriate references. However, it is true that we refuse to spread the charitable veil of goodwill and kind feelings over fallacies and false conclusions. A soft exculpatory attitude like that would only serve to perpetuate past misconceptions and to misguide future scientists.

This report ends with an outlook to further studies in thermodynamics of irreversible processes, where a systematic extension of the conventional theory is envisaged, e.g. for a phonon "gas" in crystalline solids. And there is a brief mention of liquid crystals and, – particularly –, of non-Newtonian, rheological fluids which are still in need of a thermodynamic treatment.

1 Irreversible thermodynamics before thermodynamics of irreversible processes

1.1 Abstract

Thermodynamics of irreversible processes is sometimes considered as a late arrival in the field of thermodynamics, and its emergence is dated back to the 1930's or, specifically, to the works of Onsager in 1931 and Eckart in 1939. And, indeed, those years and those scientists *are* important for the development of the theory as we shall see. However it is also true that irreversible thermodynamic processes have been treated – successfully treated – long before the word thermodynamics was even coined, which happened in or about 1850.

1.2 Phenomenological equations

Joseph Fourier's youthful ambition was to become an artillery man. That seemed to be an impossible dream at first, because Fourier's parents were poor. But then the

French revolution happened, and in the new age of *fraternité* and *égalité* Fourier was permitted to enter a military school, the later École Polytechnique. The artillery at the time had problems with the heating-up of their cannon barrels and so naturally, perhaps, Fourier studied heat conduction. He pronounced the law

$$q_i = -\kappa \frac{\partial T}{\partial x_i} \qquad (\kappa > 0) \qquad (1.1)$$

between the heat flux q_i and the temperature gradient $\frac{\partial T}{\partial x_i}$ in 1808 [Fourier 1808]. The law implies that the heat flux is opposite to the temperature gradient, or that heat flows from hot to cold, never in the opposite direction. It forms, of course, part of Fourier's great monograph "Théorie analytique de la chaleur" [Fourier 1822], which appeared in 1822, and to this day the law is called Fourier's law.

Napoléon Bonaparte was Fourier's mentor. He took Fourier along on his disastrous Egyptian campaign and later made him a baron in recognition of his great mathematical discoveries. The greatest discovery was, of course, the method of harmonic decomposition of functions, which places Fourier firmly among the greatest mathematicians of all times. That method was developed in the course of his efforts to solve the heat equation (1.2). The first to be thoroughly impressed by this powerful mathematical tool was Fourier himself, who talks about it as if he could not believe in his own ingenuity.

In addition to (1.1), Fourier derived – in a deft manner – the *heat equation*

$$\frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x_i \partial x_i} \qquad (\lambda > 0), \qquad (1.2)$$

the prototype of all parabolic equations in mathematical physics. He solved the equation for a large variety of initial and boundary conditions[3], and so it happened that complex problems of heat conduction and temperature distribution were routinely solved by engineers before anybody knew for certain what heat actually was[4]. Fourier refuses to speculate about the question: says he; *one can only form hypotheses on the inner nature of heat, but the knowledge of the mathematical laws that governs its effects is independent of all hypotheses.*

Among Fourier's solutions there is the elegant calculation of the damped temperature wave moving into the soil when its surface is subject to a periodic – daily or yearly – oscillation of temperature due to solar radiation: at a certain depth winters are warmer than summers. The impact of the Théorie Analytique was enormous; it was read everywhere, and Lord Kelvin used the results when he estimated the age of the earth from the time it should have taken the initial liquid sphere to cool to present conditions [Thomson 1862][5].

Another law for an irreversible process, – somewhat less obviously connected with thermodynamics than Fourier's law –, is the law of Navier, Poisson, and Stokes for viscous friction between the stress t_{ij} and the velocity gradient[6] $\frac{\partial v_i}{\partial x_j}$

$$t_{ij} = -p\delta_{ij} + \nu \frac{\partial v_l}{\partial x_l} \delta_{ij} + 2\eta \frac{\partial v_{<i}}{\partial x_{j>}} \qquad (\nu > 0, \eta > 0). \qquad (1.3)$$

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[3] κ and λ were called internal and external conductivities, respectively, by Fourier. Nowadays they are called the thermal conductivity and the thermal diffusivity.

[4] That knowledge came in the 1840's with the discovery of the first law of thermodynamics. E.g. [Müller 2007].

[5] That estimate was erroneous, because Kelvin was unaware of the fact that the earth is continuously heated by radioactive decomposition of constituent elements.

[6] Poisson is rarely mentioned in this context nowadays, even though his expression – with *two* viscosities – was more complete than Navier's and Stokes's who had only the shear viscosity.

where p is the pressure and ν and η are bulk- and shear viscosities, respectively. [Navier 1822; Poisson 1829; 1831; Stokes 1845].

Like Fourier, Navier and Poisson came from the École Polytechnique in Paris, a hotbed of great discoveries in mathematical physics between its foundation in 1794 and 1840. Stokes was a little later; he was the founder and first eminent representative of the English school of applied mathematics which remained influential for a century; Stokes solved the momentum balance in fairly complex circumstances, using (1.3) and the method of decomposition of functions into spherical harmonics, an extension or variant of Fourier's harmonic analysis.

Stokes was very interested in the motion of the pendulum, and in 1851 he wrote a long article on the question [Stokes 1851]. Section 2 of that article is entitled: *Solutions of the equations in the case of a sphere oscillating in a mass of fluid either unlimited, or confined by a spherical envelope concentric with the sphere in its position of equilibrium.*

The result could be specialised to the case of a sphere in an infinitely extended fluid. If the radius of the sphere is r and its constant velocity is v, the force needed to maintain the motion comes out as

$$F = 6\pi\eta r v, \tag{1.4}$$

a formula that is universally known as *Stokes's law of friction.*

The solution of boundary value problems for the Navier-Stokes fluid required more than an able mathematician. A boundary value for the tangential velocity on the sphere (say) is needed. And, hesitantly, Stokes proposes what is now-a-days called the *no-slip condition: the condition which first occurred to me to assume ... was that the film of fluid immediately in contact with the solid did not move relatively to the surface of the solid* [Stokes 1851, p. 312].

Stokes tends to consider this assumption as valid when the mean velocity of the flow is small. He was aware of the difficulties that turbulence might raise. But he was blissfully unaware, of course, of the problems that may arise in rarefied gases; these are problems that haunt the present-day researchers concerned with re-entering space vehicles.

Fluids which obey the Navier-Stokes equations (1.3) are often called *Newtonian.* And there are many of them, ranging from highly viscous honey, or asphalt, over water to rarefied ideal gases. Newton discovered a special case of the equations in the course of his study of the question whether, perhaps, the speed of the moon was affected by friction with the ether. However, of course, he did not find evidence for such an effect.

Along with Fourier's and Navier-Stokes's equations there is a third *phenomenological equation*[7] which was pronounced in the 19th century, and that concerns diffusion. It can be attributed to Adolf Fick who tried to derive the governing equation from the notion that there is gravitational (!) attraction between the molecules of a mixture [Fick 1855]. When that idea did not work particularly well, Fick had the good sense to refer to Fourier and conclude: *indeed, one will have to admit that nothing be more probable than this: the diffusion of a solute in a solvent ... follows the same rule which Fourier has pronounced for the distribution of heat in a conductor.* Thus he came to pronounce Fick's law for a binary mixture

$$J_i = -D\frac{\partial c}{\partial x_i}, \tag{1.5}$$

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[7] So called, we believe, because the laws were read off – after a fashion – from the phenomena of heat conduction, internal friction and diffusion.
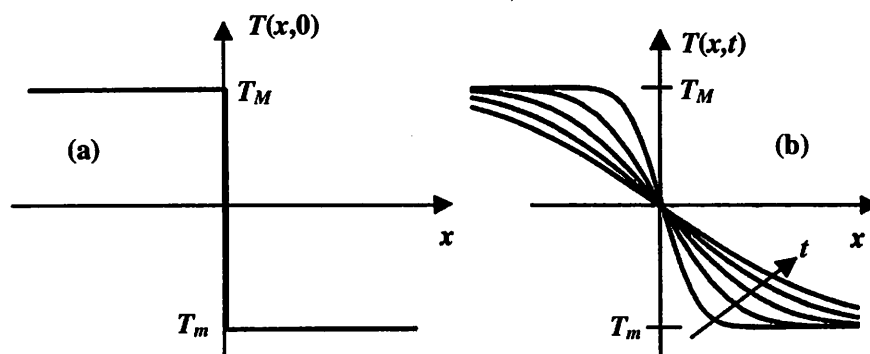
Fig. 1. Evolution of temperature between two half-spaces with initially different temperatures.

where J_i is the diffusion flux of constituent 1 and c is its concentration. D is called the diffusion coefficient. The law was quickly – and rather obviously – extended by Stefan to a mixture of ν constituents α ($\alpha = 1, 2, \ldots \nu$) [Stefan 1871].

$$J_i^\alpha = -\sum_{\alpha=1}^{\nu} D_{\alpha\beta} \frac{\partial c_\beta}{\partial x_i}. \qquad (1.6)$$

The three laws, those of Fourier, Navier-Stokes, and Fick have persisted for nearly two centuries with only minor modifications. To this day they prove their practical validity every day in the hands of engineers who construct heat exchangers, airplanes and centrifuges for the separation of constituents in gas mixtures. And yet, those phenomenological equations are not perfect from a mathematical point of view. Indeed, all three of them lead to parabolic differential equations of the type (1.2) for temperature, shear velocity[8], and concentration, respectively. That is bad, because parabolic equations imply *infinite speeds* of propagation.

For illustration let us consider an initial temperature field of the type shown in Figure 1a which is constant in the half spaces $x < 0$ and $x > 0$, but with unequal values. The solution of (1.2), arrived at by Fourier's methods, reads

$$T(x,t) = \frac{T_m + T_M}{2} + \frac{T_m - T_M}{2} \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{\lambda t}}} e^{-z^2} dz. \qquad (1.7)$$

Graphs of this function are shown for different times in Figure 1b. Inspection shows that for all $t > 0$ the temperature is affected at all points with a finite $|x|$. In a manner of speaking the initial temperature jump at $x = 0$ has made itself felt everywhere immediately, as if it had propagated to both sides with infinite speed. This phenomenon has been called the *paradox of heat conduction* and it has served as the main motivation for the formulation of *extended thermodynamics*, a recently developed theory governed by hyperbolic laws, cf. Sections 8, and 9.

The figure suggests that the temperature field is smoothed out in time and, indeed, by (1.2) the temperature rises, where the field is convex and it drops where the field is concave. It follows that the temperature field tends to become homogeneous in time, provided the boundary conditions permit that. This is the prototype of an irreversible process, because the opposite behaviour is never observed nor, indeed, can it happen in a process governed by the heat equation. *Mutatis mutandis* the same holds for shear velocity and concentration so that there are paradoxes connected with those fields as well.

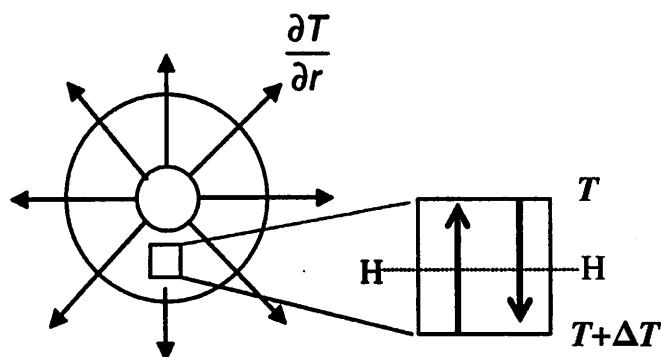[8] A typical shear velocity field is of the type $v = (v_1(x_2), 0, 0)$.

Fig. 2. On the atomistic interpretation of Fourier's law.

1.3 Atomistic interpretation of heat flux in a gas and of viscous friction

The laws of Fourier, Navier-Stokes and Fick, being motivated by observations, needed an atomistic interpretation in order to be properly *understood*. Such an interpretation – a particularly instructive one – was furnished by Maxwell in his first paper on the kinetic theory of gases [Maxwell 1860]. In order to indicate the essential features of Maxwell's derivation for the validity of Fourier's law, we consider a gas between two co-axial cylinders which are kept at different temperatures so that a radially outward temperature gradient is created. We focus the attention on a small element of the gas of the order of magnitude of a mean free path of the atoms, see Figure 2. The atoms flying inwards from the hot outer boundary of the element carry more energy in the mean than the atoms that fly outwards from the cold inner boundary. Thus, when a pair of atoms has passed the middle plane H-H – one flying inwards and one outwards – an amount of energy has also passed, and that amount is proportional to the gradient of T and opposite to it. This is just as Fourier's law predicts it.

A very similar argument can be constructed for the atomic interpretation of the viscous frictional force between two layers of a gas which move with different speeds in the same direction. In that case it is the transport of momentum – not energy – that matters. A caricature of the situation, popular with students, envisages two trains passing each other on parallel tracks. Passengers change the momenta of the trains by stepping from one to the other. Upon arrival in the new train they must support themselves against either the forward or the backward wall in order to stay on their feet. Thereby they accelerate or brake the new train depending on whether the old one was faster or slower. In the end the trains assume the same speed and we may say that: momentum exchange or *friction* has equalised the speeds.

Needless to say that the kinetic theory of gases, and Maxwell himself, have more formal arguments than these to explain both heat conduction and viscous friction, though we stick to suggestive arguments, at least for the time being, and as much as that is possible.

1.4 Irreversible processes between equilibria

Gay-Lussac was a chemist who performed a simple experiment which may be used to show that the specific internal energy u of ideal gases – which a priori might depend on density ρ and temperature T – is independent of density. The set-up and the execution of the experiment are illustrated in Figure 3: a slide-valve is opened so as to allow a compressed ideal gas to expand and flow into an initially evacuated chamber. The whole system is adiabatically isolated: the wall allows no heat flux, and it is kept at rest. The transition of the gas is a precipitous process, strongly turbulent, very inhomogeneous, and certainly – *obviously* – non-reversible. The details
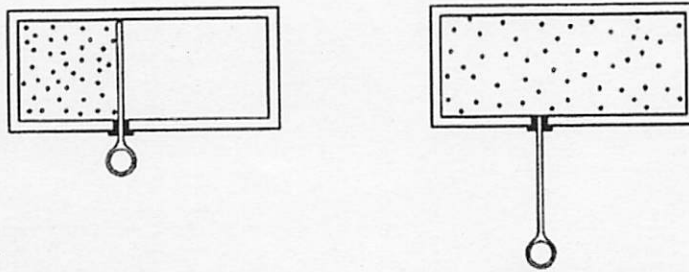
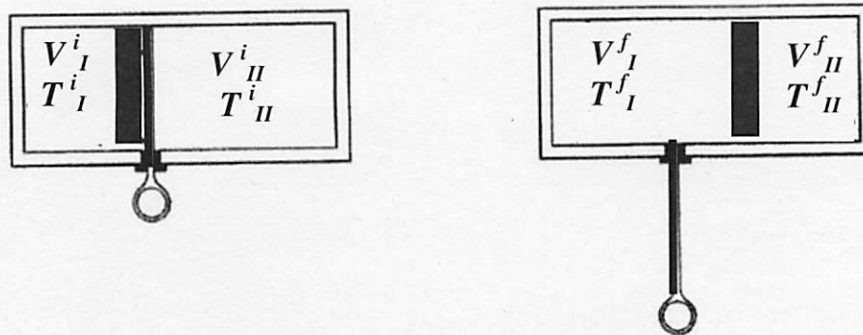**Fig. 3.** Experiment of Gay-Lussac. Initial and final states.

Fig. 4. On the "paradox" of the adiabatic plug. The final pressures are equal in the two compartments.

of the process cannot be followed, let alone calculated; except, perhaps, by elaborate numerical means, if the pull-out of the valve and the boundary values on valve and wall were exactly prescribed However, the eventual equilibrium is simple: the gas tends to a homogeneous state and Gay-Lussac observed that its final temperature *has the same value* as the initial temperature.

Several decades after Gay-Lussac, James Prescott Joule and William Thomson (Lord Kelvin) repeated the experiment with initially strongly compressed air and with Joule's superior thermometers. They found a slight cooling after the process. The cooling is due to the work done to separate the air molecules and it occurs to the extent that air is not really an ideal gas. The effect is called the Joule-Thomson effect, or Joule-Kelvin effect.

The point in mentioning these historical experiments in the present article is, of course, that they deal with irreversible processes – strongly irreversible ones – which were successfully treated by the pioneers without any help of any theory of irreversible thermodynamics, simply by comparing the initial and final equilibria. Thus, when a large number of Joule-Kelvin experiments have led to a reliable caloric equation of state $u = u(\rho, T)$, we may *predict* the state of the gas at the end of the precipitous flow, i.e. in the final equilibrium.

This simple method, however, does not always work. There is the case of the *adiabatic plug*, illustrated in Figure 4, a variant of Gay-Lussac's experiment: an initially locked piston separates two parts of the same ideal gas in given volumes and with initial temperatures $T_I^i = T_{II}^i$ (say), but under different pressures. The piston, or plug, is supposed to have an adiabatic surface, i.e. it does not permit heat transfer, nor does it change temperature itself. When it is unlocked, an irreversible process occurs in both compartments. Eventually, and after possible oscillations the plug comes to rest and a new homogeneous equilibrium occurs, with equal pressures in both compartments. In this case the final temperatures T_I^f, T_{II}^f *cannot be predicted*, because the work on the plug during the irreversible transition from the initial to the final equilibrium is unknown; it depends on the unknown and effectively unknowable details
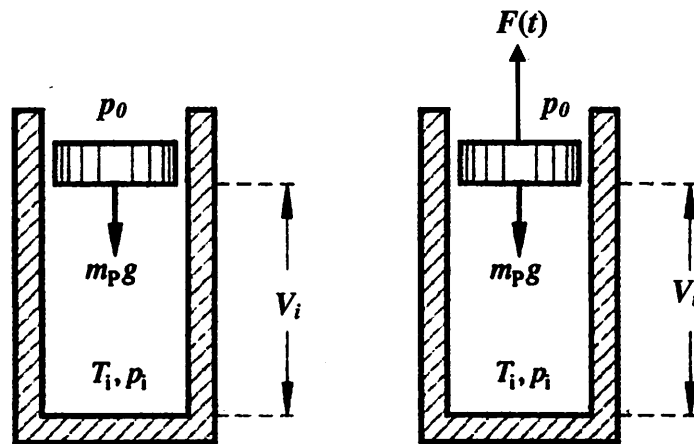
Fig. 5. Another problem with an adiabatic plug. (a) The plug falls into a gas-filled cylinder. (b) The plug is *eased* into the cylinder.

of the irreversible process which will generally differ between two experiments of this type. Callen calls this phenomenon a *uniquely delicate problem* [Callen 1960], whilst others – more bluntly – speak of the *paradox of the adiabatic plug*. In actual fact it is a true problem of irreversible thermodynamics and no theory ever developed is capable of solving it; except, perhaps, by numerical means.

Another interesting problem with an adiabatic plug, which *can* be solved by considering the initial and final equilibria, is when the plug falls into a gas-filled cylinder which is adiabatically isolated, see Figure 5a. The gravitational potential energy of the plug is then converted into internal energy and the gas heats up. Given the initial volume of the cylinder and the initial values of the temperature of the gas, one may use the known equations of state for a monatomic gas to calculate the final values of those quantities [Müller 2009, pp. 38/39].

$$T_f = \frac{3}{5}T_i \left(1 + \frac{3}{5}\frac{p_0 + \frac{m_P g}{A}}{p_i} \right), \qquad V_f = \frac{2}{5}V_i \left(1 - \frac{3}{2}\frac{p_i}{p_0 + \frac{m_P g}{A}} \right). \qquad (1.8)$$

A is the cross-sectional area of cylinder and plug and m_P is the mass of the plug. p_i is the initial pressure in the cylinder. Of course, the fall of the plug induces a strongly irreversible process inside the air of the cylinder and no theory of irreversible thermodynamics is adequate to calculate the details of the process. Nor do they matter as long as we are only interested in the final state. A surprising aspect, perhaps, of the problem occurs in the limiting case of an infinitely heavy plug: the final temperature is infinite in that case while, however, the volume remains finite, i.e. non-zero.

In the case of the falling plug, see Figure 5, we can make the process reversible by controlling the fall so as to make it very slow. In that case the gas remains virtually homogeneous, no turbulence, internal friction and heat conduction of any significance occur, and the state of the gas changes adiabatically and *reversibly*. That is to say that, upon subsequently pulling out the plug slowly, we let the process in the gas run through its former states in the reverse direction. The control of the motion of the plug may be achieved by applying an appropriate force $F(t)$ which keeps the plug and the gas nearly in equilibrium during the fall or ascent (see Fig. 5b). The volume, pressure, and temperature of the gas during the reversible process are then related by what thermodynamicists call the *adiabatic equations of state*

$$pV^{5/3} = p_i V_i^{5/3} \qquad \text{or} \qquad \frac{p}{T^{\frac{5}{2}}} = \frac{p_i}{T_i^{\frac{5}{2}}} \qquad \text{or} \qquad VT^{\frac{3}{2}} = V_i T_i^{\frac{3}{2}}. \qquad (1.9)$$

If the plug is infinitely heavy – making the final pressure infinite – the final volume of the gas *now* obviously tends to zero, while the temperature tends to infinity as before.

The notion of easing the falling plug so slowly into the cylinder, that the state of the gas changes *reversibly*, may seem like an improbable artifice. And yet, that artifice has proved to be immensely practical and heuristically useful, because a large part of engineering thermodynamics relies on that notion. The question is: how slow is slow? And it turns out that even the processes in the engine of a Formula I racing car, with 18 000 revolutions per minute, are slow enough for reversibility, at least in a good approximation. Indeed, the large speeds of the pistons in such a car are still much slower than the speed of sound, and that speed of sound determines the homogenisation process of the gas in the working cylinder[9].

Thus, when books on technical thermodynamics report efficiencies of engines like[10]

$$e_{Steam\ engine} = 1 - \frac{Q_{Condenser}}{Q_{Boiler}}, \quad e_{Otto\ engine} = 1 - \frac{1}{\varepsilon^{\kappa-1}}, \quad e_{Carnot\ engine} = 1 - \frac{T_{Cooler}}{T_{Boiler}},$$

(1.10)

the shortfall of the efficiency from the value 1 is *not* due to irreversibility; indeed, all of the efficiencies (1.10) refer to reversible processes. The ubiquitous unpreventable irreversibility – due to turbulent flow, internal friction and heat losses by conduction – has been neglected in the derivation of (1.10). Its effect practically *cannot be calculated*, except numerically, but we do know that it decreases the efficiencies to values below those given in (1.10).

2 Entropy and the nature of entropic growth in irreversible processes

2.1 Abstract

The mid-19th century saw the discovery of the equations of balance of energy and entropy, the so-called first and second laws of thermodynamics. The former is a conservation law for all processes in a body and the latter is an inequality to the extent that the process under consideration is irreversible. The history of the discovery of those two laws has been thoroughly investigated, and described in many places, e.g. see [Müller 2007], and will therefore not be part of the present article which is focussed on irreversibility. Suffice it to say that Clausius's discovery of the entropy balance was based on the axiom

heat cannot pass by itself from a colder to a warmer body,

which was extrapolated from observations about heat conduction, see Section 1. That fairly loose statement was ingeniously exploited by Clausius. Thus he obtained the specific expression (1.10)$_3$ for the efficiency of a reversible Carnot engine, which Carnot himself, and Clapeyron, and Kelvin had sought in vain. And he arrived at the concept of entropy.

Boltzmann, through his work on the kinetic theory of gases, see Section 7, was able to *define* entropy in terms of the probability of the distribution of atoms in random

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[9] The slowness of the moving parts in an internal combustion engine compared to the speed of sound is not the only reason for the applicability of reversible thermodynamics in such engines. Another one is the supply of a fresh, undisturbed gas mixture during every stroke. We do not discuss that aspect.

[10] Q is the heat exchanged, and ε – in the case of the four-stroke Otto engine – is the compression ratio. κ is the ratio of specific heats at constant pressure and constant volume.

thermal motion. The definition is such that it can easily be extrapolated away from ideal gases. Thus an entropic growth was linked to the probability of a distribution in *any* random process, not necessarily the homogenisation of a gas when it approaches equilibrium irreversibly. Indeed, we may now speak of the increase of entropy of a polymer chain as it contracts under thermal motion, or of the increase of entropy in the adjustment of a species to the environment in an evolutionary process subject to random mutation.

Boltzmann's probabilistic interpretation of entropy and entropy growth met with strong opposition and Boltzmann's defense did not satisfy everybody. Nor has it convinced all physicists to this day. They have, however, blanked out the objections. Simple mechanical models, however, keep the questions open; notably the consideration of mass-spring chains for which reversibility and an apparent approach to equilibrium can be discussed in an explicit manner.

2.2 The two laws of thermodynamics. Entropy and energy

Thermodynamics is based on the First and Second Laws. The first law is the conservation law of energy - internal energy U, potential energy E_{pot}, and kinetic energy K - and it states that the rate of change of energy of a body in the volume V equals the sum of heating $\dot{Q}$ and working $\dot{W}$ on the surface ∂V of the body[11]

$$\frac{d\left(U + E_{pot} + K\right)}{dt} = \dot{Q} + \dot{W}, \quad \text{where} \quad \dot{Q} = -\int_{\partial V} q_i n_i dA \quad \text{and} \quad \dot{W} = \int_{\partial V} t_{ij} v_i n_j dA.$$

(2.1)

The second law is an inequality about the rate of change of entropy S, and it states

$$\frac{dS}{dt} = -\int_{\partial V} \frac{q_i n_i dA}{T} + \Sigma, \quad \text{where} \quad \Sigma \geq 0.$$

(2.2)

Σ is the entropy production; it vanishes when the process in the body is reversible. The second law in the form (2.2) is called the Clausius-Duhem inequality; Clausius had considered a special case only, for which the temperature is homogeneous on ∂V, or on *the* part of ∂V where heat exchange occurs. Duhem generalised the law to arbitrary temperature fields on ∂V; thus providing the possibility of converting the entropy balance into a local equation.

Since the *inequality* (2.2) holds for an irreversible process, we may say that the entropy production *measures* the irreversibility. In an adiabatic body, where $q_i = 0$ holds on ∂V, the entropy production is equal to the rate of change of entropy. Thus the entropy of an adiabatic body tends to a maximum in an irreversible process. The maximum is reached at *equilibrium*, when the irreversible "mechanisms" heat conduction, internal friction and diffusion have led to homogeneous fields of temperature, and chemical potentials, and to vanishing velocity; and when chemical reactions have come to an end.

This observation was the motivation for Clausius's doctrine of the *heat death*. Says he: *it is often said that the world goes in a circle... such that the same states are always reproduced. Therefore the world could exist forever. The second law of thermodynamics contradicts this idea most resolutely ... The entropy tends to a maximum. The more closely that maximum is approached, the less cause for change exists. And when the maximum is reached, no further changes can occur; the world is then in a dead stagnant state* [Clausius 1867].

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[11] n_i is the outer unit normal on the surface of V. t_{ij} and q_i are stress and heat flux, as before, while v_i is the velocity.

That idea was much discussed in the 19th and early 20th century. One of the more colourful comments was the one by Oswald Spengler, philosopher and historian, and author of the book "The Decline of the West": *the end of the world as the completion of an inevitable evolution – that is the twilight of the gods* [of Germanic mythology]. *Thus the doctrine of entropy is the last, irreligious version of the myth* [Spengler 1917].

The physicist Josef Loschmidt deplored ... *the terroristic nimbus of the second law ..., which lets it appear as a destructive principle of all life in the universe* [Loschmidt 1876; 1877; 1878].

Loschmidt was a keen observer of the developing thermodynamics of his time. As a scientist he is credited with finding an approximate value of the Avogadro number [Loschmidt 1865]. And indeed, in Germany and Austria, where Loschmidt lived, that number is often called the Loschmidt number.

Although (2.2) does not *define* entropy, the law may be used to *calculate* the entropy S of a body in equilibrium. Thus for a reversible process in a fluid, i.e. a sequence of equilibria, where $\dot{W} = -p\frac{dV}{dt}$ holds, provided that E_{pot} is zero or constant, we may eliminate $\dot{Q}$ between (2.1) and (2.2) and obtain the *Gibbs equation*[12]

$$\frac{dS_E}{dt} = \frac{1}{T}\left(\frac{dU}{dt} + p\frac{dV}{dt}\right). \qquad (2.3)$$

So, if the caloric equation of state $U = U(V,T)$ and the thermal equation of state $p = p(V,T)$ are known, we may calculate $S_E = S_E(V,T)$ by integration of the Gibbs equation to within an additive constant. In particular, for a monatomic ideal gas we obtain

$$S_E(V,T) = Nk\left[\ln\left(VT^{3/2}\right) + \text{const.}\right]. \qquad (2.4)$$

N is the number of atoms and k is the Boltzmann constant.

2.3 Available free energy

If a body is not adiabatic, but rather subject to other boundary conditions, there is in general not any quantity that approaches an extremum, because the irreversible processes do not come to an end under the new boundary conditions. However, there are special boundary conditions for which this *is* the case. The best-known one – and most important one, perhaps – occurs when the boundary ∂V is at rest and the temperature on the boundary is homogeneous and constant in time; we denote it by T_0. In that case $\dot{W}$ vanishes, and we may then eliminate $\dot{Q}$ between (2.1) and (2.2) to come up with the new inequality

$$\frac{d\left(U + E_{pot} + K - T_0 S\right)}{dt} = -T_0 \Sigma \leq 0. \qquad (2.5)$$

We express this by saying that the available free energy, or *availability A*, tends to a minimum under those isothermal conditions

$$A = U + E_{pot} + K - T_0 S \rightarrow \text{minimum}. \qquad (2.6)$$

Physicists like to say that A decreases, when the body is immersed in a *heat bath*.

We conclude from (2.6) that a decrease of energy is conducive to an equilibrium and so is an increase of entropy: if T_0 – the temperature of the heat bath is small,

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[12] The index E on S stands for equilibrium. The equation was first derived and exploited by Clausius. But Gibbs extended it to mixtures of fluids and exploited it fully.

the availability decreases, because the energy $U + E_{pot} + K$ tends to a minimum. But if T_0 is large, the availability decreases, because the entropy tends to a maximum. In general, i.e. for intermediate values of T_0, it is neither the energy which becomes minimal, nor the entropy which becomes maximal. The two tendencies compromise and thus equilibrium is characterised by a minimal availability.

All this is crystal-clear, and the mathematics leading to (2.6) is trivial, but it did not seem so to scientists of the 19th century, even eminent ones. There were the energeticists, led by Friedrich Wilhelm Ostwald, who maintained that the entropy is not needed and that equilibrium is characterised by a minimum of energy. Boltzmann fought them with Planck as an unappreciated ally [Planck 1970], and in the end, – after the main contenders were dead – the entropic contribution was universally recognised.

In order to anticipate a misunderstanding we stress that the availability in (2.5), (2.6) is *not* the Helmholtz free energy, since the temperature field inside the body may not be homogeneous and hence may not be equal to T_0.

However, the availability *is indeed* equal to the free energy of Helmholtz when the transition to equilibrium has proceeded so far in a body that temperature is already homogeneous, while other fields have not yet reached their equilibrium values. Alternatively, if one disturbs an equilibrium maintaining homogeneous temperature, the free energy must necessarily increase. Minimal free energy thus characterises a stable equilibrium and that requirement leads to all the conventional stability conditions like positive specific heats, positive compressibilities, etc.

Now, leaving this subject, and without wishing to belittle Clausius's contribution to thermodynamics, we dare say – somewhat provocatively – that Clausius did not know what entropy was. Indeed, the second law in the form (2.2) represents a *property* of entropy, not a *definition*. Such a definition in terms of atoms or molecules was found by Boltzmann not long after Clausius's discoveries.

2.4 Statistical definition of entropy

Boltzmann's definition of entropy is now usually written in the form

$$S = k \ln W, \tag{2.7}$$

where W is the number of possibilities to realise a distribution of atoms or molecules.

We proceed to illustrate that definition in the simplest possible manner which we have found useful for explaining the definition of entropy to students. Thus we consider a monatomic gas with N atoms of mass μ sitting on the P occupiable points in a volume V[13]. The distribution of atoms is then given by $\{N_1, N_2, \ldots N_P\}$, where N_i ($i = 1, 2, \ldots P$) is the number of atoms on point i. The surface ∂V has the temperature T kept constant by a heat bath.

By the rules of combinatorics the number of realisations of that distribution is given by

$$W = \frac{N!}{\prod\limits_{i=1}^{P} N_i!} \qquad \text{hence} \qquad S = k \ln \frac{N!}{\prod\limits_{i=1}^{P} N_i!}. \tag{2.8}$$

In order to motivate and interpret this definition of entropy we must ask whether it implies the properties of Clausius's entropy. In particular, does it have the growth property? And does its maximum, the equilibrium value, depend on V and T as in

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[13] We take the points as discrete and discuss that assumption in a short while. Also: the velocities of the atoms play no role in the distribution. Sometimes in statistical mechanics the entropy based on that simplified distribution is called the *configurational entropy*. This serves us well, at least for the present arguments.

equation (2.4)? Indeed, it does and, in order to see this we must make one observation and two reasonable assumptions [Boltzmann 1886; Broda 1979].

The observation concerns thermal motion. We know that the atoms of the gas move – on average over time or over many atoms – with a kinetic energy $\frac{\mu}{2}\bar{c}^2$ of the order of magnitude $\frac{3}{2}kT$ so that, for T as room temperature, the mean speed $\bar{c}$ amounts to several hundred meters per second. Consequently the realisations of a distribution and – generally – a distribution itself change very quickly. We assume that each and every realisation of N atoms on the P points in V occurs just as often as any other one. For instance the case when all N atoms are on a single point *occurs just as often* as the case when the first N/P atoms lie on point 1, the next N/P ones lie on point 2, ... and the last N/P atoms lie on point P. That seems to be the only reasonable unbiased assumption given the random character of the thermal motion, and it is known as the a priori assumption of equal probability for the realisations. It means, of course, that a distribution with many realisations is more likely to occur than a distribution with fewer realisations, and the most probable distribution is that with the most realisations which, by (2.8), is the homogeneous equi-distribution $N_i = N/P$ $(i = 1, 2, \ldots P)$.

So, what about growth? Suppose that initially all N atoms lie on a single given point. That distribution can only be realised in *one* manner, so that $W = 1$ holds and $S = 0$. The thermal motion, however, will quickly mess up that orderly distribution and, in all probability, lead to distributions with more realisations, i.e. positive entropies and, eventually, to the equi-distribution with most realisations, i.e. maximal entropy. Such is the nature of the entropic growth toward equilibrium! Obviously that kind of growth is probabilistic and not necessarily irreversible, but the reverse process – leading from more probable distributions back to less probable ones – is extremely unlikely. It becomes more and more unlikely when more and more atoms are involved. Thus for $N \approx 10^{23}$ atoms in one litre – a common gas density – the irreversible growth of entropy is virtually certain. Other than Boltzmann, Gibbs was one of the first scientists to understand this and he says: ... *the impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability* [Gibbs 1876, p. 229].

This is not to say that momentarily the entropy cannot decrease for a short while. The overall approach to a maximal entropy may well be briefly interrupted by a *fluctuation*. And even in equilibrium – the eventual equi-distribution of maximal entropy – there may be fluctuations toward less probable distributions. Thus equilibrium is not really a "dead stagnant state" as Clausius had thought when he considered the heat death.

In equilibrium with the equi-distribution $N_i = N/P$ $(i = 1, 2, \ldots P)$, and close to equilibrium with $N_i \approx N/P$, we obtain from $(2.8)_2$[14]

$$S_E(P) = Nk\ln P \quad \text{and} \quad S(P, N_i) = k\left(N\ln P - \frac{P}{N}\frac{1}{2}\sum_{i=1}^{P}\left(N_i - \frac{N}{P}\right)^2\right). \quad (2.9)$$

So, in order to know the entropy, we have to determine P, the number of occupiable points in V. We assume, or take it for granted, that P is proportional to V and write

$$P = \alpha V \quad (2.10)$$

so that $1/\alpha$ represents the volume which can accommodate *one* point. We may say that $1/\alpha$ quantises the volume and, again, it was Boltzmann who introduced that

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[14] Here and elsewhere below we adopt the Stirling formula $\ln n! = n\ln n - n$ to replace the factorial expressions in (2.8). This represents the *classical* approach. For alternatives see [Schrödinger 1948], or also [Müller 2007].

notion. However, he dismisses it as a mathematical trick. He considers it *needless to emphasise that* (in writing $P = \alpha V$) *we are not concerned with a real physical problem, ... the assumption is nothing more than an auxiliary tool* [Boltzmann 1872].

Thus Boltzmann narrowly missed opening up a possible access to quantum mechanics. He was too timid. Later Planck made quantisation acceptable and de Broglie discovered that atoms could be considered as waves which – roughly – need a volume proportional to the cube of the wave length $\lambda = \frac{h}{\mu \bar{c}}$, the de Broglie wave length[15]. In equilibrium the mean speed of an atom in a gas of temperature T is $\bar{c} = \sqrt{3 \frac{k}{\mu} T}$ so that – in the mean – an atom needs at least a cubic box of dimension

$$\frac{1}{\alpha} = \left(\frac{h}{\sqrt{\mu\, 3kT}} \right)^3 \quad \text{hence} \quad P = V T^{3/2} \left(\frac{\sqrt{\mu 3k}}{h} \right)^3 \quad \text{and}$$

$$S_E = Nk \left(\ln V T^{3/2} - \ln \left(\frac{h}{\sqrt{\mu 3k}} \right)^3 \right). \quad (2.11)$$

This form of S_E compares well with (2.4) thus confirming that Boltzmann's definition of entropy coincides with Clausius's entropy: it has the growth property and the equilibrium values agree. The indeterminate additive constant in Clausius's entropy is now seen to depend on the Planck constant[16]. Also we see that the number P of points in V does not change in a reversible adiabatic process, according to the adiabatic equation of state, see $(1.9)_3$.

Boltzmann's formula $S = k \ln W$ may be extrapolated away from gases to any other system consisting of many identical elements subject to the random thermal motion. It may even be applied to economic and ecological systems which exhibit some randomness *not* due to thermal motion. Thus for instance random mutations in a population of cells may be shown to produce an irreversible evolution toward proper adjustment to an environment, e.g. see [Müller 2010].

2.5 Controversies

Boltzmann's atomistic and probabilistic interpretation of the growth of entropy did not go unopposed. Rather it started a long-lasting controversy which, if the truth were known, has never been concluded. There were two major objections: the *recurrence argument* and the *reversibility argument*.

The recurrence argument was presented by Zermelo, a student of Max Planck's, who involved Boltzmann in an acrimonious public debate [Zermelo 1896a; 1896b; Boltzmann 1896a; 1896b]. The argument relied on a theorem of analytical mechanics, proved by Poincaré, according to which a finite system of atoms must perform a quasi-periodic motion which recurs arbitrarily close to its initial state arbitrarily often [Poincaré 1890]. Rather obviously this prediction contradicted a monotonic growth of entropy which, after all, is determined by the atomic positions. Boltzmann answered by pointing out, that the expected recurrence time was nearly infinitely large – much, much larger than the age of the universe. Zermelo was unimpressed, but most physicists to this day are resigned to the argument. See also the argument in Section 2.6 below.

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[15] h is the Planck constant, and μ and $\bar{c}$ are mass and mean speed of the atoms as before.
[16] Although (2.11) takes the quantum mechanical nature of the atoms into account by assigning them a de Broglie wave length, it ignores another aspect of quantum mechanics, namely the indistinguishability of atoms. Therefore the equation implies a non-additive entropy. We leave it at that for the time being. The correct formula will be given in Section 7, see (7.19).

The reversibility argument was raised by Josef Loschmidt, the person who coined the phrase about the *terroristic nimbus of entropy* [Loschmidt 1876]. He argued that the motion of atoms is reversible. They may just as well run forward and backwards according to Newton's laws. And, if the entropy increased in one direction, it should decrease in the other direction. Thus Loschmidt concluded that the entropy should equally frequently increase and decrease. Boltzmann responded that there are many, many more disordered distributions of atoms than ordered ones. Thus when we start in an ordered distribution, the entropy-increasing transition order → disorder should nearly always occur.

That reply never convinced anybody, not even Boltzmann himself. It seems like a reformulation of the assumption of a priori equal probability. Indeed, the question remained why there should be more initial conditions leading to growth than the other type. And so, eventually Boltzmann came up with a suggestion which is either science-fiction or far ahead of his – and our – time. Says he: ... *in the universe which is nearly everywhere in equilibrium, and therefore dead, there must be small regions of the size of our stellar space which, during the relatively short period of eons, deviate from equilibrium and among these equally many in which the probability of states increases and decreases. ... A creature that lives in such a period and in such a world will denote the direction of time toward less probable states as the past, the opposite direction as the future* [Boltzmann 1896b].

Thus the growth of entropy in a decaying fluctuation was linked to the inexorable progress of time and so was the subsequent decrease of entropy in the build-up of a new fluctuation: the apparent contradiction was resolved by Boltzmann – in a manner of speaking – by considering the direction of time as a psychological delusion. In this view time objectively runs forward and backwards equally often, while subjectively, in our brains, it runs always in the direction of entropic growth.

Boltzmann was quick to take the sting out of this mind-boggling idea about time in the fluctuations of the universe: *Surely nobody will consider a speculation of that sort as an important discovery or – as the old philosophers did – as the highest aim of science. It is, however, the question whether it is justified to scorn it as something entirely futile.*

Still, we may suspect that Boltzmann was not entirely sincere when he made that disclaimer. Indeed, over the years he repeated this interpretation of time and fluctuations of the universe several times. After having invented it in the discussion with Zermelo, he repeats it, and expands on it in his book on the kinetic theory [Boltzmann 1895] and, again, in his lecture at the World Fair in St. Louis [Boltzmann 1904]. So we may conclude that he trusted the idea at least to the extent that he was sure that nobody could expose it as stupid, – at least not quickly[17].

2.6 The one-dimensional linear mass-spring chain as a mechanical paradigm for recurrence, reversibility and – irreversibility of a sort

The one-dimensional chain of N masses m and $N-1$ springs with stiffness $1/\lambda$ shown in Figure 6 may serve as an illustrative purely mechanical example for recurrence and reversibility in a system of many particles. Ironically the system can also be seen as exhibiting irreversibility and damping. The advantage of the chain over gases is that all calculations can be done explicitly and analytically.

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[17] Boltzmann attempts to make the suggestion more acceptable by drawing an analogy to the subjective notions of "up" and "down" on the earth, where two persons in antipodes both think that they stand right-side-up, while objectively one of them is upside-down.
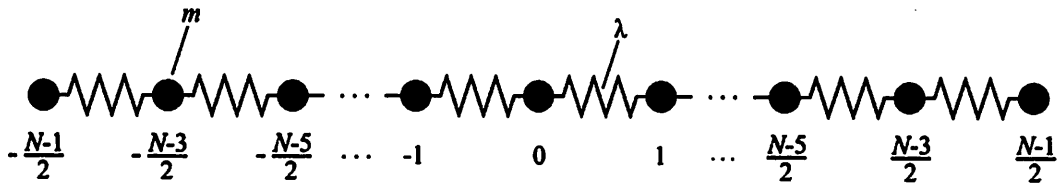
Fig. 6. The linear chain of masses m and springs with stiffness $1/\lambda$.

Let $u_\beta(t)$ be the displacement of mass β ($\beta = -\frac{N-1}{2}, -\frac{N-3}{2}, \ldots, -1, 0, 1, \ldots,$ $+\frac{N+1}{2}$) from its original value shown in the figure[18]. Thus there is a central mass with the displacement $u_0(t)$. The equations of motion read

$$\ddot{u}_\beta(t) = \sum_{\gamma=-\frac{N-1}{2}}^{\frac{N-1}{2}} a_{\beta\gamma} u_\beta, \quad \text{where} \quad a_{\beta\gamma} = \frac{\lambda}{m}\begin{bmatrix} -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 & 0 & 0 \\ - & - & - & - & - & - & - \\ - & - & - & - & - & - & - \\ 0 & 0 & 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 \end{bmatrix},$$

and, of course, they are coupled because of next-neighbour interaction. Uncoupling by an orthogonal transformation

$$u_\beta(t) = \sum_{s=0}^{N-1} O_{\beta s}^T q_s \quad \Leftrightarrow \quad q_s = \sum_{\beta=-\frac{N-1}{2}}^{\frac{N+1}{2}} O_{s\beta} u_\beta$$

is possible. It leads to $N-1$ harmonic eigen-vibrations plus a translation, viz. $q_0(t) = q_0(0) + \dot{q}_0(0)t$ and

$$q_s(t) = q_s(0)\cos\omega_s t + \frac{1}{\omega_s}\dot{q}_s(0)\sin\omega_s t, \quad (s = 1\ldots N-1).$$

Thus the solutions $u_\gamma(t)$ for the initial value problem $\{u_\beta(0)|\dot{u}_\beta(0)\}$ read

$$u_\gamma(t) = \frac{q_0(0)}{\sqrt{N}} + \frac{\dot{q}(0)}{\sqrt{N}}t + \sum_{s=1}^{N-1} O_{\gamma s}^T \left(q_s(0)\cos\omega_s t + \frac{1}{\omega_s}\dot{q}_s(0)\sin\omega_s t\right)$$

$$u_\gamma(t) = \frac{1}{N}\sum_{\beta=-\frac{N-1}{2}}^{\frac{N-1}{2}} (u_\beta(0) + \dot{u}_\beta(0)\, t)$$

$$+ \sum_{\beta=-\frac{N-1}{2}}^{\frac{N-1}{2}} \sum_{s=1}^{N-1} O_{\gamma s}^T O_{s\beta} \left(u_\beta(0)\cos\omega_s t + \frac{1}{\omega_s}\dot{u}_\beta(0)\sin\omega_s t\right). \tag{2.12}$$

The frequencies $\omega_s = 2\sqrt{\frac{\lambda}{m}}\sin\frac{s\pi}{2N}$ ($s = 0, 1, 2, \ldots, N-1$) are the eigen values of the matrix $a_{\beta\gamma}$ and $O_{\beta s}^T = \sqrt{\frac{b_s}{N}}\cos(N-2\beta)\frac{s\pi}{2N}$ $b_s = \begin{cases} 1 \\ 2 \end{cases}$ for $s = \begin{cases} 0 \\ \text{else} \end{cases}$ are the corresponding eigen-vectors of that matrix.

Obviously the vibrational motion $u_\beta(t)$ cannot be periodic if all eigen vibrations $s \neq 0$ are present, since many frequencies are irrational numbers[19]. However,

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[18] N needs to be an odd number in that nomenclature.

[19] Even for $N = 3$, where we have only two eigen-vibrations with $\omega_1 = \sqrt{\frac{\lambda}{m}}$ and $\omega_2 = \sqrt{3\frac{\lambda}{m}}$, periodicity is impossible, since the numbers 1 and $\sqrt{3}$ are non-commensurable.

quasi-periodicity is possible and, indeed, unavoidable. A quasi-period, or recurrence occurs at a time t when all $\{q_s(t)|\dot{q}_s(t)\}$ are in a close neighbourhood of their initial values $\{q_s(0)|\dot{q}_s(0)\}$. Thus $u_\beta(t)$ will be close to $u_\beta(0)$ for all β, and that might be good enough to consider the original state reproduced, a circumstance which Claudius *most resolutely* said was impossible, see Section 2.2.

An estimate of the recurrence time has been presented by Hemmer [Hemmer 1959]. He let $q_s(t)$ and $\frac{1}{\omega_s}\dot{q}_s(t)$ $(s = 1, 2, \ldots N - 1)$ span a vector space so that the position and velocity of an eigen vibration may be represented by the circular rotation of the tip of an arrow $v_s = (q_s, \frac{1}{\omega_s}\dot{q}_s)$ – with angular frequency ω_s. If the arrows initially point into the directions φ_s, a recurrence time T_R of the chain is defined as the time when *all* the rotating arrows $v_s(T_R)$ $(s = 1, 2, \ldots N - 1)$ point into the angle element between φ_s and $\varphi_s + \Delta\varphi$ for some small $\Delta\varphi$. By an ingenious argument Hemmer shows that – on average over many recurrences – the recurrence time is equal to

$$T_R = \left(\frac{2\pi}{\Delta\varphi}\right)^{N-2} \frac{1}{\frac{1}{2}\text{ctg}\frac{\pi}{4N} - 1} \frac{\pi}{\sqrt{\frac{\lambda}{m}}} \underset{N \gg 1}{\approx} \left(\frac{2\pi}{\Delta\varphi}\right)^{N-2} \frac{\pi^2}{2N\sqrt{\frac{\lambda}{m}}}.$$

If we take $\sqrt{\frac{\lambda}{m}} = 10^{13}\frac{1}{s}$ as a typical atomic vibrational frequency in a metallic lattice, and choose $\Delta\varphi = \frac{\pi}{100}$, we obtain very large numbers for $N = 21$ and $N = 101$ respectively, namely $T_R^{21} = 3.98 \times 10^{22}a$ and $T_R^{101} = 9.83 \times 10^{205}a$. In both cases – even for such relatively few masses – the recurrence times are many times longer than the estimated age of the universe; in the second case, for $N = 101$, they are unimaginably longer! So we may say that, for practical purposes the motion of the chain is not reversible; instead, it *seems* irreversible for a long, long time, because it does not come back during that time.

However irreversibility usually means more to us than non-recurrence. Indeed, the notion of irreversibility is connected in our minds with the decay of a system to a homogeneous state, e.g. the damping of differences in temperature, velocity and chemical potentials. And, indeed, the chain exhibits damping of sorts too; at least it exhibits a phenomenon that seems like damping. In order to see that, we consider the special case in which only the central mass $\beta = 0$ has an initial displacement – $u_0(0)$ and all masses are initially at rest. In that case, by (2.12) we have

$$u_\gamma(t) = \left(\frac{1}{N} + \sum_{s=1}^{N-1} O_{\gamma s}^T O_{s0} \cos\omega_s t\right) u_0(0). \tag{2.13}$$

Figure 7 shows a plot of this solution for $N = 201$ and for the central mass $\gamma = 0$. At first that mass appears to experience a damped oscillation which comes to an end when reflections from the ends of the chain interfere, which happens at time $\sqrt{\frac{\lambda}{m}}t \approx 200$. After that the values of $u_0(t)$ seem to fluctuate randomly and the seemingly random nature becomes more pronounced for larger-time intervals, e.g. for $2000 \le \sqrt{\frac{\lambda}{m}}t \le 2200$, as indicated in the figure. It can be established by numerical calculations that for those large-time intervals the mean potential and kinetic energies of the masses fluctuate around equal shares of the initial energy. That observation suggests *equipartition of energy*, a well-known property of equilibrium in statistical thermodynamics. This behaviour might well be misinterpreted as the result of irreversible dissipation of the initial energy. As it is, however, we do know that eventually the apparent irregular fluctuation reorganises itself and re-establishes the initial state of the chain as closely as we wish, albeit after a long – very long(!) – time.
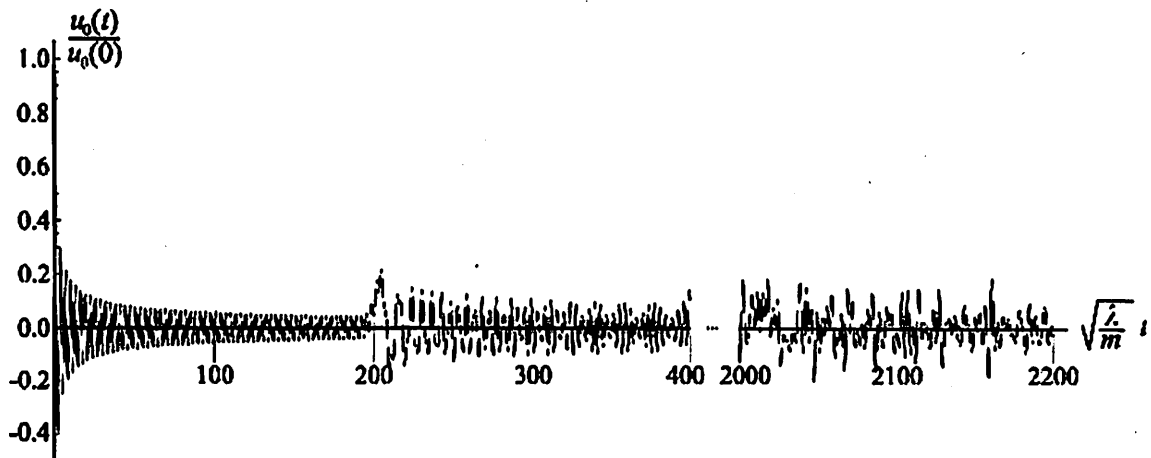
Fig. 7. Apparent approach of the central mass to a seemingly random fluctuation for the initial value problem $\{u_\gamma(0)|\dot{u}_\gamma(0)\} = \{0, 0, \ldots, 0, u_0(0), 0, 0 \ldots 0|0, 0, 0 \ldots 0\}$.

The situation is different, of course, for $N \to \infty$: For infinitely many chain links the recurrence time is obviously infinite and the solutions (2.13) can easily be shown to tend to

$$u_\gamma(t) = \left[\frac{2}{\pi} \int_0^{\frac{\pi}{2}} \cos 2\gamma x \cos\left(2\sqrt{\frac{\lambda}{m}}t \sin x\right) dx \right] u_0(0) = J_{2\gamma}\left(2\sqrt{\frac{\lambda}{m}}t\right) u_0(0).$$

$$(2.14)$$

$J_{2\gamma}(2\sqrt{\frac{\lambda}{m}}t)$ are Bessel functions which are well known to decay to zero for $t \to \infty$ in an orderly oscillatory – non-fluctuating – manner. Obviously there are no reflections at the ends either.

To those for whom damping means *exponential* decay we may say that even that behaviour may be had in the chain, albeit after a slight modification: if the chain is given a central mass $M \gg m$, and if it has infinitely many links, the initial displacement $u_0(0)$ decays exponentially. For reference we cite Magalinskij, Turner, Rubin and Müller's review of those research works, which was conducted in an effort to understand irreversibility [Magalinskij 1959; Turner 1960; Rubin 1960; Müller 1962].

Everything is explicit in the chain and fully deterministic. And we can confirm that Loschmidt was right: if at some time T, even a large time, the values $u_\gamma(T)$ are registered as new "initial" conditions and the velocities $\dot{u}_\gamma(T)$ are changed into $-\dot{u}_\gamma(T)$, the graph of Figure 7 is travelled through backwards for $t > T$; i.e. in particular it proceeds from the small-amplitude fluctuations of $u_0(t)$ to larger amplitudes, and the value $u_0(0)$ is reached at $t = 2T$. This behaviour can easily be confirmed on the computer.

2.7 Still a dilemma?[20]

For one and a half centuries much has been said about the controversies between Boltzmann, Zermelo and Loschmidt, and we are sure that we cannot contribute to the subject in an essential and original manner. Still, we wish to say this, a remark that has probably been made by others before: on the foregoing pages we have identified

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[20] Quantum mechanical considerations are not part of this report. They may or may not help with the dilemma, if there is a dilemma.

two conceivable interpretations of irreversibility, namely

- a gas in a heat bath - i.e. with an isothermal boundary - experiences an irregular thermal motion of the atoms which makes it assume new distributions with many different realisations every split second. We assumed equal probability for all realisations, and thus came to the concept of a *probable* growth of entropy $S = k \ln W$. Recurrence of an initial state is possible, since the initial realisation of the initial distribution has a non-zero probability, albeit a small one, - the same probability as any other realisation.
- the chain of springs and masses, on the other hand, experiences a fully deterministic motion of all oscillators once given the initial condition $\{u_\gamma(0)|\dot{u}_\gamma(0)\} = \{0, 0, \ldots, 0, u_0(0), 0, 0 \ldots, 0, |0, 0, 0 \ldots, 0\}$; there is no real random motion in this completely isolated system. The initial condition can only be realised in *one* manner, so that $W = 1$ and $S = 0$ hold. The entropy is zero and it remains zero, because the number of realisations of subsequent states is again one; after all, there is a one-to-one relation between the initial values and later ones. Therefore, whatever approach to apparent randomness in Figure 7 we may feel occurs in the chain, it is not accompanied by a growth of entropy. And if near-infinite recurrence times of the chain are interpreted as *effective* irreversibility, that type of irreversibility is not accompanied by entropic growth.

So, what about the universe, whose entropy Clausius so confidently predicted was growing because it was subject neither to heating nor to working, and therefore growing in entropy at constant energy? If indeed the universe was isolated in that manner, it would be like our chain, - without heat bath and true random thermal motion -, and its motion would be deterministic and the entropy would be constant and equal to zero. The heat death is then not a viable proposition and recurrence is certain, albeit in a very distant future.

2.8 Entropies galore

Some specific differential equations studied by mathematicians exhibit a growth property that is faintly reminiscent of entropic growth and has therefore led to a plethora of "entropies", all unrelated to heating and working or to any probabilistic interpretations.

An easy example is the motion of the central mass of the linear chain when it has infinitely many links. By (2.14), and for the proper initial conditions of the chain, its motion $u_0(t)$ is represented by the Bessel function $J_0(t)$, so that it must satisfy Bessel's differential equation[21]

$$\ddot{u} + \frac{1}{t}\dot{u} + u = 0. \tag{2.15}$$

This equation does not suggest irreversibility in any way[22] and yet we know that $u(t)$ is some kind of damped oscillation, namely the Bessel function of *zero*th order. And indeed, multiplication of the equation by $\dot{u}$ and some juggling provides an inequality for the quantity

$$\eta(u, \dot{u}) = \eta(0, 0) - \frac{1}{2}u^2 - \frac{1}{2}\dot{u}^2, \quad \text{namely} \quad \dot{\eta} \equiv \frac{\dot{u}^2}{t} \geq 0. \tag{2.16}$$

So, if growth were all that counted, we might be tempted to call η an entropy.

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[21] The index zero on u is now dropped.

[22] In particular, the inversion of time $t \to -t$ leaves the equation unchanged.

Another instructive example is provided by the Burgers equation with a damping term on the right hand side, the prototype of a hyperbolic equation of first order, viz.

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} = -\beta u \quad (\beta > 0). \tag{2.17}$$

Multiplication by u and, again, some easy juggling of terms gives

$$\frac{\partial \left(-\frac{u^2}{2}\right)}{\partial t} + \frac{\partial \left(-\frac{u^3}{3}\right)}{\partial x} = \beta u^2 \geq 0. \tag{2.18}$$

This equation has the form of an equation of balance, complete with a density $-\frac{u^2}{2}$, a flux $-\frac{u^3}{3}$, and a non-negative production βu^2, like the thermodynamic entropy.

Of course, we may ask whether there is any good reason to consider such "entropies". The answer is: yes, there is, because mathematicians find them useful in order to prove asymptotic results concerning the solution of their equations for large times.

Take the one-dimensional heat equation, for instance, with boundary and initial conditions:

$$\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial x^2} \quad \text{with} \quad \frac{\partial T}{\partial x}(x = \pm L, t) = 0 \quad \text{and} \quad T(x, t = 0) = T_0(x). \tag{2.19}$$

The stationary solution is obviously

$$T_\infty = \frac{1}{2L}\int\limits_{-L}^{+L} T_0(x)\, dx,$$

and now the question might be asked whether the solution of (2.19) tends to T_∞ in time for all $T_0(x)$. This is indeed the case, and it is proved by the observation that the rate of change of the "entropy"

$$H = \int\limits_{-L}^{+L} F\left(\frac{T - T_\infty}{T_\infty}\right) T_\infty dx \quad \text{for any convex function } F \tag{2.20}$$

has a sign; it is negative. Take for instance $F(\chi) = \chi^2$. It is then easy to show that

$$\frac{\partial H}{\partial t} = -\frac{2\lambda}{T_\infty}\int\limits_{-L}^{+L}\left(\frac{\partial(T - T_\infty)}{\partial x}\right)^2 dx \leq 0$$

holds[23]. Hence follows by Poincaré's inequality[24]

$$\frac{\partial H}{\partial t} \leq -\frac{2\lambda c}{T_\infty}\int\limits_{-L}^{+L}(T - T_\infty)^2\, dx = -2\lambda c H.$$

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[23] Quantities like this, – with a rate of a definite sign –, are sometimes called H-functions, because Boltzmann gave his entropy the Greek letter *eta*, whose capital form is H.

[24] Poincaré's inequality reads $\int(\frac{\partial f}{\partial x})^2 dx \geq c\int f^2 dx$ for a function f with $\int f dx = 0$; the constant c depends on L.

Thus it turns out, albeit not trivially, that we have $H(t) \le H(0) \exp(-2\lambda ct)$, so that $H(t \to \infty) = 0$, hence $T(t \to \infty) = T_\infty$; this completes the proof.

"Entropies" like (2.20) are sometimes called Kullback entropies [Kullback 1951]. They were introduced in the context of information theory. And they have nothing at all to do with the physical entropy, neither the one of Clausius nor Boltzmann's. One cannot help wishing that a different term – rather than entropy – had been chosen. That might have helped to avoid unfounded analogies which lead to confusion.

3 Fluctuations and Onsager relations

3.1 Abstract

This report moves forward roughly chronologically, so that Onsager is next. His reciprocity relations gained him the Nobel prize, although they are based on a most daring hypothesis about the mean regression of fluctuations. Also, in the pertinent literature after Onsager, the reciprocity relations were extrapolated far beyond the point where even that daring hypothesis can be applied.

If Onsager's reciprocity relations are true, there are two attractive corollaries: the orthogonality condition, by which the entropy production determines the rate of change of the non-equilibrium variables, and the principle of least energy dissipation.

Let the historians of science be warned: this is not an account of what Onsager wrote, because what Onsager wrote is unpalatable and largely indigestible. It is not for nothing that his papers [Onsager 1931a; 1931b] were refused when he offered them as a doctoral thesis to his home university in Trondheim, Norway. Even his otherwise fairly obsequious biographers Longuet-Higgins and Fisher have to report that [Longuet-Higgins 1991]. So what we present here is largely due to the careful interpretation of Onsager's works by de Groot and Mazur, slightly modified by ourselves [de Groot 1962]. We dare say, however, that the reader – whether physicist or historian – can learn more here about Onsager's arguments than he could from Onsager's works themselves.

3.2 Macroscopic relaxation laws

We consider a model for a gas in the state N_i ($i = 1, 2, \ldots P$), i.e. with N_i atoms on P points. The gas is in a heat bath which keeps the temperature of the boundary constant and homogeneous. That model was used in Section 2.4 to explain the configurational entropy and the growth of entropy during the process leading from an initial distribution $\{N_1^0, N_2, \ldots N_P\}$ to the equi-distribution $N_i = N/P$. Actually the model may not be the best one physically to demonstrate a relaxation process toward equilibrium, but heuristically it is useful for us, because it may serve as a paradigm for the exhibition of an irreversible process – and we already know it. In particular we know its entropy close to equilibrium, cf. $(2.9)_2$. The rate of change of entropy follows by differentiation

$$\frac{dS}{dt} = -k\frac{P}{N} \sum_{i=1}^{P} \left(N_i - \frac{N}{P}\right) \frac{dN_i}{dt}. \tag{3.1}$$

The right hand side is the entropy production Σ and, by (2.2), it must be non-negative. We satisfy this requirement by assuming a relaxation law of the form

$$\frac{dN_i}{dt} = -\sum_{k=1}^{P} R_{ik} \left(N_k - \frac{N}{P}\right), \qquad \text{where } R_{ik} \text{ is positive definite.} \tag{3.2}$$
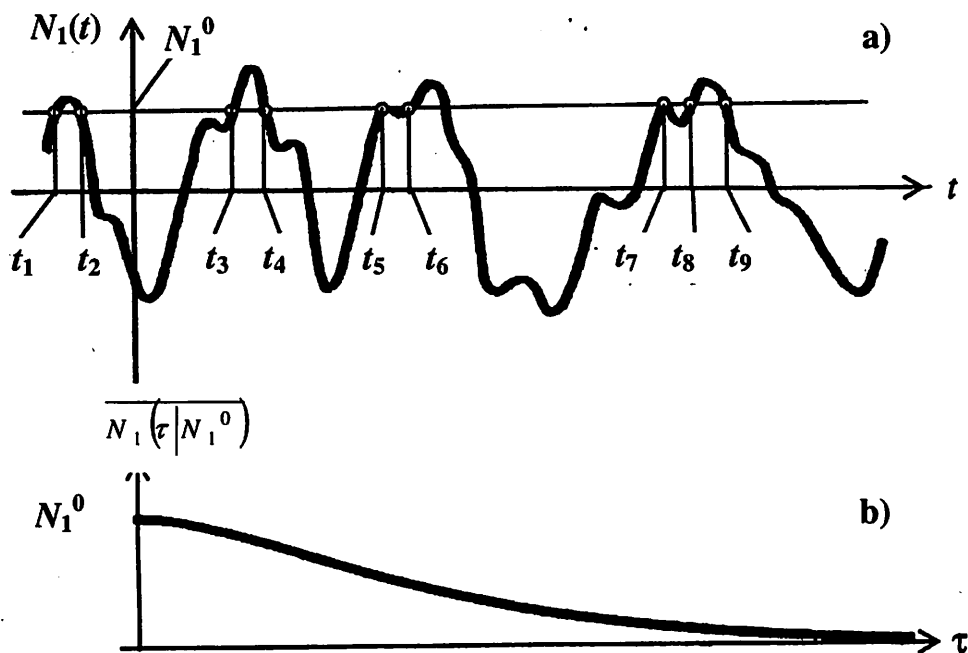
Fig. 8. (a) Fluctuation of $N_1(t)$. (b) Mean regression of a fluctuation N_1^0 of N_1.

The formal solution reads

$$N_i(t) - \frac{N}{P} = \sum_{k=1}^{P} \exp\left(-R_{ik}t\right) \left(N_k^0 - \frac{N}{P}\right) \quad (i = 1, 2, \ldots P). \tag{3.3}$$

We may consider (3.2) as a phenomenological law abstracted from the observation of a relaxation process in a gas by a macroscopic observer and consistent with the second law. The macroscopic observer sees no fluctuations and he perceives the eventual equi-distribution as constant, or as *stagnant* to use Clausius's formulation.

3.3 Fluctuations

In reality, however, there are fluctuations, both during the relaxation process and in the eventual equilibrium, and we could see them, if we were equipped with a sufficiently powerful microscope, and if we were able to resolve the rapid rates of change of the fluctuating N_i's. Onsager has considered fluctuations *in equilibrium* and he used a chain of arguments about those fluctuations in order to suggest that the relaxation matrix R_{ik} in (3.2) is symmetric [Onsager 1931a; 1931b]. We proceed to explain these arguments and to assess them.

3.3.1 Gaussian character of fluctuations

First of all, there is a profound difference between a macroscopic relaxation toward equilibrium and a fluctuation around equilibrium: the former is irreversible and makes the N_i's tend to constant values, while the latter never comes to rest and seems to be reversible in its gross features. Figure 8a shows a graph for a single fluctuating N_i – for $i = 1$ (say) – as a function of time in some interval. This fluctuation continues forever and remains unchanged in its practically non-smooth and rapidly changing

random character. To be sure, the details of the fluctuating curve are different over previous and subsequent time intervals so that predictions can only be probabilistic.

It stands to reason that the probability of a distribution $\{N_1, N_2, \ldots N_P\}$ is proportional to the number of possibilities to realise that distribution which, by (2.7), is given by

$$W = \exp \frac{S}{k}, \quad \text{hence, by } (2.9)_2$$

$$p(N_1, \ldots N_P) = \frac{1}{\sqrt{2\pi N/P}^P} \exp\left(-\frac{P}{N}\frac{1}{2}\sum_{i=1}^{P}\left(N_i - \frac{N}{P}\right)^2\right), \quad (3.4)$$

provided that N_i is close to N/P which we confidently expect for a microscopic fluctuation near equilibrium. Thus the probability $p(N_1, N_2, \ldots N_P)$ is a Gaussian, and we may use it to calculate mean values or expectation values

$$\overline{N_i} = \frac{N}{P}, \quad \text{and} \quad \overline{\left(N_i - \frac{N}{P}\right)\left(N_k - \frac{N}{P}\right)} = \frac{N}{P}\delta_{ik}. \quad (3.5)$$

3.3.2 Microscopic reversibility

Reversibility for the fluctuation means that we see another realistic fluctuation when we look at the mirror image of the graph of Figure 8a, if the mirror is held perpendicular to the time axis. That reversibility is a consequence of the reversibility of the thermal motion which makes the atoms fly in any direction and the opposite one equally often, and which causes the fluctuation of the distribution. From this it follows that

> the probability of seeing $\{N_1^0, \ldots, N_P^0\}$ at some time and $\{N_1, \ldots, N_P\}$ at a time τ later is equal to the probability of seeing $\{N_1, \ldots, N_P\}$ at some time and $\{N_1^0, \ldots, N_P^0\}$ at a time τ later.

Formally we may write this in the form

$$p\left(N_1^0, \ldots, N_P^0\right) P\left(N_1^0, \ldots, N_P^0 | N_1, \ldots, N_P, \tau\right) = p(N_1, \ldots, N_P)$$

$$\times P\left(N_1, \ldots, N_P | N_1^0, \ldots, N_P^0, \tau\right), \quad (3.6)$$

where $P(N_1, \ldots, N_P | N_1^0, \ldots, N_P^0, \tau)$ is a conditional probability. It is the probability to see the distribution $\{N_1^0, \ldots, N_P^0\}$ at some time *provided that* the distribution was $\{N_1, \ldots, N_P\}$ at a time τ earlier. Unlike $p(N_1, \ldots, N_P)$ the conditional probability is unknown.

Equation (3.6) is the requirement of reversibility of fluctuations. Onsager places a strong emphasis upon this assumption and he discusses it at length. Upon reflection, the assumption seems to be a safe conclusion – hardly worthy of so much emphasis. It is an inescapable consequence of the never-ending and reversible random character of the thermal motion of the atoms which causes the fluctuations.

3.3.3 Mean regression

In contrast to this, Onsager's main assumption, – the assumption about the mean regression of a fluctuation – is barely mentioned by him, and certainly not critically

assessed, although the assumption is a steep one, and difficult to accept. Let us consider this now.

We repeat that there is no sign of irreversibility in fluctuations. They continue forever, and remain unchanged in their random character; and certainly they show no decay. And yet, it is possible to detect an element of smoothness and decay within the fluctuations, if one constructs the *mean regression* of a given fluctuation of size $\{N_1^0, \ldots, N_P^0\}$ averaged over many occurrences. This is a function of τ defined in terms of the conditional probability as

$$\overline{\left(N_i(\tau) - \frac{N}{P}\right)}^{\{N_1^0 \ldots N_P^0\}} \equiv \sum_{N_1=0}^{N} \ldots \sum_{N_P=0}^{N} \left(N_i - \frac{N}{P}\right) P\left(N_1^0, \ldots N_P^0 \mid N_1, \ldots N_P, \tau\right).$$

(3.7)

Since an assumption about mean regression is a crucial point in Onsager's argument, we define the function again – in a more suggestive and less formal manner than by (3.7) – by constructing it from Figure 8a, albeit for a single fluctuating variable N_1 (say): we consider ν times t_α ($\alpha = 1, 2, \ldots \nu$) for which N_1 has a given fixed value N_1^0 and register the values $N_1(t_\alpha + \tau)$ at a time τ after t_α. Then we form the average over those later occurrences

$$\overline{N_1(\tau)}^{N_1^0} = \frac{1}{\nu} \sum_{\alpha=1}^{\nu} N_1(t_\alpha + \tau).$$

(3.8)

This is the mean regression function of a fluctuation N_1^0; it is called a *regression* because, whenever the construction is carried out for any observed fluctuating quantity, the resulting curve is decaying as shown qualitatively in Figure 8b.

Onsager's hypothesis is that the mean regression of a fluctuation is equal to the relaxation of a macroscopic deviation $\{N_1^0, N_2^0, \ldots N_P^0\}$ from the equi-distribution. Thus, by (3.7) and (3.3) he postulates

$$\overline{\left(N_i(\tau) - \frac{N}{P}\right)}^{\{N_1^0 \ldots N_P^0\}} = \sum_{k=1}^{P} \exp\left(-R_{ik}\tau\right) \left(N_k^0 - \frac{N}{P}\right).$$

(3.9)

Now, that hypothesis deserves a comment and it has received many. Let us be brief and quote only S.R. de Groot and P. Mazur, two authors sympathetic to Onsager, who wrote the most-often-cited textbook on non-equilibrium thermodynamics [de Groot 1962]. They say on p. 102 of the book with regard to Onsager's hypothesis (3.9): *the hypothesis that the equation ... is correct for small values* [of $(N_i - N/P)$] *does not seem altogether unreasonable...* Well, that is faint praise indeed. It seems hard to think of a more damaging comment and still remain within the confines of the soft-spoken politeness expected from a scientific evaluation.

Anyway, whether the hypothesis (3.9) is valid or not, one thing is clear. It applies to rate laws and relaxation processes, not to transport equations like Fourier's law for the heat flux. We shall comment on that point below, in Sections 3.5 and 4.

Let us add just one more point. The hypothesis (3.9) is quite obviously wrong for small times τ, since the macroscopic relaxation is exponential, – starting out at $\tau = 0$ with a negative slope, while the mean regression function must be *even* in τ with a vanishing derivative at $\tau = 0$. This must be so, because the fluctuations at the times t_α ($\alpha = 1, 2, \ldots \nu$) go up and down equally often, if ν is large enough. Onsager himself recognises that and he attempts to anticipate criticism on that point in a page-long discussion in which, interestingly, there are overtones of extended thermodynamics, cf. Sections 8 and 9. However the discussion is not specific and remains inconclusive.

Physicists and chemists passionately believe in Onsager's arguments, all the more so, the less they understand them. And we, the authors of this article, are ambivalent. We believe – indeed, it comes down to beliefs (!) – that Onsager's hypothesis on mean regression is true, despite its daring character and despite the non-existent proof. The basis for our confidence is experimental evidence gathered in the field of light scattering, which is due to density fluctuations, see Section 9.

3.3.4 Symmetry relation

The final argument is simple now and above reproach, if the hypothesis on mean regression is accepted. As a starting point we combine (3.7) and (3.9) to obtain

$$\sum_{k=0}^{P} \exp\left(-R_{ik}\tau\right) \left(N_k^0 - \frac{N}{P}\right) = \sum_{N_1=0}^{N} \ldots \sum_{N_P=0}^{N} \left(N_i - \frac{N}{P}\right) P\left(N_1^0, \ldots N_P^0 \middle| N_1, \ldots N_P, \tau\right).$$

We multiply both sides by $(N_l^0 - N/P)p(N_1^0, \ldots N_P^0)$ and form the sums $\sum_{N_1^0=0}^{N} \ldots \sum_{N_P^0=0}^{N}$. This provides us with the possibility to employ the requirement of reversibility (3.6) and to use the specific mean values (3.5)$_2$. Despite their formal complexity we write the four lines of intermediate calculation down in a frame, so as to give the interested reader the possibility to follow the argument, and the not so interested one to skip it and to proceed to (3.10).

$$\sum_{k=0}^{P} \exp\left(-R_{ik}\tau\right) \sum_{N_1^0=0}^{N} \ldots \sum_{N_{P_1}^0=0}^{N} \left(N_k^0 - \tfrac{N}{P}\right)\left(N_l^0 - \tfrac{N}{P}\right) p\left(N_1^0 \ldots N_P^0\right) =$$

$$\sum_{N_1=0}^{N} \ldots \sum_{N_P=0}^{N} \sum_{N_1^0=0}^{N} \ldots \sum_{N_P^0=0}^{N} \left(N_i - \tfrac{N}{P}\right)\left(N_l^0 - \tfrac{N}{P}\right)$$

$$\times p\left(N_1^0 \ldots N_P^0\right) P\left(N_1^0 \ldots N_P^0 \middle| N_1 \ldots N_P, \tau\right)$$

$$\tfrac{N}{P} \exp\left(-R_{il}\tau\right) = \sum_{N_1=0}^{N} \ldots \sum_{N_P=0}^{N} \sum_{N_1^0=0}^{N} \ldots \sum_{N_P^0=0}^{N} \left(N_i^0 - \tfrac{N}{P}\right)\left(N_l - \tfrac{N}{P}\right)$$

$$\times \underbrace{p\left(N_1 \ldots N_P\right) P\left(N_1 \ldots N_P \middle| N_1^0 \ldots N_P^0, \tau\right)}_{p\left(N_1^0 \ldots N_P^0\right) P\left(N_1^0 \ldots N_P^0 \middle| N_1 \ldots N_P, \tau\right)}$$

$$= \sum_{k=0}^{P} \exp(-R_{lk}\tau) \sum_{N_1^0=0}^{N} \ldots \sum_{N_P^0=0}^{N} \left(N_i^0 - \tfrac{N}{P}\right)\left(N_k^0 - \tfrac{N}{P}\right) p\left(N_1^0 \ldots N_P^0\right)$$

$$= \tfrac{N}{P} \exp\left(-R_{li}\tau\right).$$

It follows that we must have

$$R_{ik} = R_{ki}. \tag{3.10}$$

This symmetry relation is called Onsager's reciprocity relation. It implies that the rate of change of N_i caused by a non-equilibrium value of N_k is equal to the rate of N_k

due to a deviation of N_i from its equilibrium value. *Notabene*: R_{ik} are macroscopic coefficients. Primarily, i.e. as introduced in (3.2), they have nothing at all to do with fluctuations. That is what makes Onsager's hypothesis so spectacular.

Microscopic reversibility, i.e. reversibility of the atomic motion in a body must be qualified when the body is subject to a magnetic field, or when it rests in a non-inertial frame so that either the Lorentz force or the Coriolis force – or both – affect the motion of the atoms. It is then possible that the relaxation matrix R_{ik} depends on the magnetic flux density B and on the angular velocity ω of the frame. We do not go into detail; suffice it to say that in such cases the symmetry condition (3.10) must be replaced by the relation $R_{ik}(B, \omega) = R_{ki}(-B, -\omega)$. That qualification is part of Onsager's papers of 1931.

3.4 Two corollaries of Onsager relations. Dissipation potential and principle of least energy dissipation

The reciprocity relation (3.10) has two easy corollaries which, to some people, suggest an extrapolation away from the model of the gas with the distribution $\{N_1, N_2, \ldots N_P\}$ and toward an arbitrary body whose non-equilibrium variables may generically be called α_i $(i = 1, 2, \ldots P)$.

3.4.1 First corollary. Dissipation potential, entropy production, and orthogonality condition

The entropy production Σ may be written as a function of N_i[25]. Thus, by (3.1), (3.2) we have

$$\Sigma = k\frac{P}{N} \sum_{i,k=1}^{P} R_{ik} \left(N_i - \frac{N}{P}\right)\left(N_k - \frac{N}{P}\right). \tag{3.11}$$

Differentiation with respect to N_i and the use of (3.2) gives

$$\frac{\partial \Sigma}{\partial N_i} = -2k\frac{P}{N}\frac{dN_i}{dt}, \quad \text{hence} \quad 2\Sigma = \sum_{i=1}^{P}\left(N_i - \frac{N}{P}\right)\frac{\partial \Sigma}{\partial N_i}, \tag{3.12}$$

if and only if R_{ik} is symmetric. Indeed, note that only the symmetric part of R_{ik} affects the entropy production Σ, so that the rate law, or relaxation law (3.12)₁ does not contain the anti-symmetric part either. Equation (3.12)₂ represents Euler's law for a homogeneous function of grade 2.

The extrapolation to an arbitrary body with non-equilibrium variables α_i $(i = 1, 2, \ldots P)$ – instead of $(N_i - N/P)$ – is now obvious:

There exists a positive valued entropy production $\Sigma(\alpha_i)$, homogeneous of grade 2,

such that the relaxation rates $\dfrac{d\alpha_i}{dt}$ are given by $\dfrac{d\alpha_i}{dt} = -\dfrac{1}{2}\dfrac{\partial \Sigma}{\partial \alpha_i}.$ $\tag{3.13}$

Homogeneity of the entropy production means $\Sigma = \sum\limits_{i,k=1}^{P} L_{ik}\alpha_i\alpha_k$ so that, by (3.13)₂ the rate law $\frac{d\alpha_i}{dt} = -\sum\limits_{i=1}^{P} L_{ik}\alpha_k$ holds with a symmetric and positive definite matrix L_{ik}.

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[25] Onsager and much of the literature following him prefer to speak of the dissipation potential Φ which is essentially equal to the entropy production Σ: we have $\Sigma = 2\Phi$.

The entropy production is a popular concept among applied mathematicians and mechanicians when they are interested in unspecified non-equilibrium *internal variables* α_i. They like to foreshorten thermodynamics by saying that the properties of a body are dictated by two scalar functions: the free energy for reversible processes and the entropy production – or dissipation potential – for irreversible ones.

A sometimes helpful visualisation of the formulae involving the entropy production, particularly (3.13), is the orthogonality condition to which Ziegler has called attention [Ziegler 1977; 1983]. Let us consider that proposition: in the P-dimensional space spanned by the variables α_i the entropy production $\Sigma(\alpha_i)$ – or the dissipation potential – has fixed values on a hypersurface, actually a hyperellipsoid. By (3.13) – when the α_i's are given – the corresponding rates of change $\frac{d\alpha_i}{dt}$ are orthogonal to that surface. Ziegler and the members of his group, e.g. Wehrli, have considered cases in which the entropy production is akin – in simple cases even equal – to the yield function of a plastic body [Ziegler 1987]. In that case the variables are the principal strains, at most three of them. And Ziegler's orthogonality condition may then imply the *normality rule* which is often used by plasticians to determine the plastic strain under complex two- or three-dimensional loading conditions. We are not aware though that such ideas have helped much in the complex field of plasticity, nor do they seem to be generally accepted. However, research in this field is on-going, e.g. see some recent work by Hackl [Hackl 2008].

3.4.2 Second corollary. Principle of least dissipation of energy, or least entropy production

The second corollary of Onsager's reciprocity relations concerns the entropy production Σ again. In order to explain we stick to the "internal" variables α_i – whatever they are – and write

$$\Sigma = \sum_{i,k=1}^{P} L_{ik}\alpha_i\alpha_k \quad \text{so that, by (3.13),} \quad \frac{d\alpha_i}{dt} = -\sum_{k=1}^{P} L_{ik}\alpha_k \qquad (3.14)$$

holds. It is easy to see that Σ has a *minimum under the constraint that the rates* $\frac{d\alpha_i}{dt}$ *are fixed.* Indeed, we use Lagrange multipliers λ_i to take care of the constraint and differentiate the function

$$\Sigma - \sum_{i=1}^{P} \lambda_i \left(\frac{d\alpha_i}{dt} + \sum_{k=1}^{P} L_{ik}\alpha_k \right) = \sum_{i,k=1}^{P} L_{ik}\alpha_i\alpha_k - \sum_{i=1}^{P} \lambda_i \left(\frac{d\alpha_i}{dt} + \sum_{k=1}^{P} L_{ik}\alpha_k \right) \quad (3.15)$$

with respect to α_i without constraint. The first derivative vanishes because of the constraint and the second derivative is equal to L_{ik} which is positive definite. Onsager calls this the *principle of least dissipation of energy*[26].

The principle is often dubbed PME – principle of minimal entropy production – and under that name it is frequently seriously abused in modern thermodynamics. Indeed, most authors neglect the constraint which makes it valid – and makes it fairly trivial to boot. Prigogine in particular has vastly extrapolated the idea of minimum entropy production by postulating its validity for stationary processes, and he has popularised it in his books for the general public, where the PME is embedded somewhere between Anaxagoras and Lenin [Prigogine 1983]. We shall come back to Prigogine's axiom later – in order to *disprove* it, see Section 4.2.4.

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[26] In the older literature the entropy production is quite often called energy dissipation. We consider both expressions as synonymous.

3.5 Onsager relations for heat conduction

The model of a gas with the distribution $\{N_1, \ldots N_P\}$ has served us well for the explanation of Onsager relations for rate laws and relaxation equations of the type (3.2), and (3.3). And indeed – apart from the precarious Onsager hypothesis itself – the physics and mathematics seem sound. However, this is *not* what Onsager did. In his papers he considered a transport phenomenon, namely heat conduction in a non-isotropic body, where the thermal conductivity is a tensor, and where the Fourier law is generalized to the form

$$q_i = -\kappa_{ik}\frac{\partial T}{\partial x_k} \quad \text{with} \quad \kappa_{ik} - \text{positive definite.} \tag{3.16}$$

Onsager set out to show that the tensor κ_{ik} is symmetric and so he arrived somehow at the primordial reciprocity relation $\kappa_{ik} = \kappa_{ki}$.

The derivation is hard to follow and we believe that the implied assumptions and suggestions are impossible to evaluate critically and render them convincing. Here again, de Groot and Mazur have made a heroic effort to clarify ideas and to prove what is provable [deGroot 1962]. Their reasoning is ingenious and it culminates in the conclusion that the divergence of the anti-symmetric part of κ_{ik} must vanish

$$\frac{\partial \left(\kappa_{ik} - \kappa_{ki} \right)}{\partial x_i} = 0. \tag{3.17}$$

Thus, no conclusion about the anti-symmetric part is reached when κ_{ik} is independent of x_i, although that is the most usual case considered by irreversible thermodynamic; it is in fact the *only* case considered in *linear* irreversible thermodynamics. Anyway, certainly (3.17) does not mean that κ_{ik} is symmetric.

4 Thermodynamics of irreversible processes, the doctrine of forces and fluxes

4.1 Abstract

Until about 1940 the phenomenological equations of Fourier, Fick and Navier-Stokes were disjoint pieces of knowledge, apparently unrelated. It was Eckart who joined them in a systematic and – to some extent – harmonious thermodynamic theory. That theory might be called the doctrine of forces and fluxes. It is quite simple and it refers to single fluids as well as to mixtures of fluids. Therefore it has become popular with physicists and chemists all over the world. The theory is taught everywhere where irreversible thermodynamics is on the curriculum, and it is generally known by the acronym TIP, for thermodynamics of irreversible processes.

4.2 Single fluids

Slowly in the first half of the 20th century it was recognised that thermodynamics could be interpreted as a field theory for the determination of the fields of mass density $\rho(x_i, t)$, velocity $v_j(x_i, t)$, and temperature $T(x_i, t)$ in a body. Jaumann and Lohr advertised that view [Jaumann 1911; Lohr 1926], and Eckart brought it to a conclusion of sorts [Eckart 1940a]. We proceed to describe Eckart's theory for single fluids in this section.

4.2.1 Equations of balance

For the determination of the fields $\rho(x_i, t)$, $v_i(x_i, t)$, and $T(x_i, t)$ we need field equations and these are based on the equations of balance of mechanics and thermodynamics, viz. the conservation laws of mass, momentum and energy

$$\frac{d\rho}{dt} + \rho \frac{\partial v_i}{\partial x_i} = 0 \qquad \rho \frac{dv_j}{dt} - \frac{\partial t_{ji}}{\partial x_i} = 0 \qquad \rho \frac{du}{dt} + \frac{\partial q_i}{\partial x_i} = t_{ij} \frac{\partial v_i}{\partial x_j}. \tag{4.1}$$

These laws are also known as the continuity equation, Newton's equation of motion, and the first law of thermodynamics, respectively. They are not – in this form – field equations for $\rho(x_i, t)$, $v_i(x_i, t)$, and $T(x_i, t)$, because of the occurrence of the specific internal energy u, the heat flux q_i, and the stress t_{ij}. Therefore those latter quantities must be related to the fields $\rho(x_i, t)$, $v_i(x_i, t)$, and $T(x_i, t)$ and – upon reflection – it is clear that the relations depend on the *constitution* of the material of the body; we call them *constitutive relations* or – sometimes – *phenomenological equations*.

4.2.2 Balance of entropy

Eckart motivated the form of the constitutive equations from the Gibbs equation (2.3) for a reversible process, applied to an infinitesimal mass element

$$\frac{ds}{dt} = \frac{1}{T} \left(\frac{du}{dt} - \frac{p}{\rho^2} \frac{d\rho}{dt} \right). \tag{4.2}$$

He assumed that s, u, and p are functions of ρ and T and, in fact, the same functions as in equilibrium. This is known as the *assumption of local equilibrium*. It means that locally – and instantaneously – in an irreversible process the mass elements are in equilibrium. Rather obviously, if this were true at all, it can only be true, or nearly true, if the process is *close to equilibrium*, i.e. if the rates of change are slow and the gradients are small[27]. And so, Eckart's theory is sometimes called *linear irreversible thermodynamics*: the constitutive functions can at most be linear in rates and gradients, and the theory is therefore not expected to be valid for rapid rates and steep gradients.

Elimination of the rates of u and ρ between $(4.1)_{1,3}$ and (4.2) gives after some rearrangement

$$\rho \frac{ds}{dt} + \frac{\partial}{\partial x_i} \left(\frac{q_i}{T} \right) = q_i \frac{\partial \left(\frac{1}{T} \right)}{\partial x_i} + \frac{1}{T} t_{\langle ij \rangle} \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} + \frac{1}{T} \underbrace{\left(\frac{1}{3} t_{ll} + p \right)}_{\equiv -\pi} \frac{\partial v_k}{\partial x_k}. \tag{4.3}$$

π, defined by the brace in (4.3), is the dynamic pressure, the non-equilibrium part of $\frac{1}{3} t_{ll}$.

Equation (4.3) has the form of an equation of balance of entropy. Therefore we interpret

$\varphi_i \equiv \frac{q_i}{T}$ as the entropy flux, and

$$\sigma \equiv q_i \frac{\partial \left(\frac{1}{T} \right)}{\partial x_i} + \frac{1}{T} t_{\langle ij \rangle} \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} + \frac{1}{T} \left(\frac{1}{3} t_{ll} + p \right) \frac{\partial v_k}{\partial x_k} \text{ as the density of entropy production.}$$

$$\tag{4.4}$$

---

[27] Otherwise s, u, and p may be expected to depend on (say) gradients and rates of temperature and/or velocity.

We may express $(4.4)_2$ by saying that there are three *mechanisms* of dissipation – or entropy production – in a single fluid, namely heat conduction and internal friction. The latter consists of two parts: friction by shearing and friction by isotropic expansion or compression.

By the second law the entropy production density is expected to be non-negative, since the entropy must grow in an adiabatic process.

4.2.3 Thermodynamic forces and fluxes

Inspection shows that the entropy production density is a sum of products of *thermodynamic fluxes* and *thermodynamic forces*, so called by Eckart. They are

thermodynamic fluxes	and	*thermodynamic forces*
heat flux q_i		temperature gradient $\dfrac{\partial T}{\partial x_i}$
deviatoric stress $t_{\langle ij \rangle}$		deviatoric velocity gradient $\dfrac{\partial v_{<i}}{\partial x_{j>}}$
dynamic pressure π		divergence of velocity $\dfrac{\partial v_l}{\partial x_l}$.

It is obvious that the inequality $\sigma \geq 0$ can be satisfied by letting fluxes be proportional to forces with factors of proportionality of specific signs. Hence

$$q_i = L\frac{\partial \frac{1}{T}}{\partial x_i} \qquad L \geq 0 \qquad \text{Fourier}[28] \tag{4.5}$$

$$t_{\langle ij \rangle} = 2\eta\frac{\partial v_{<i}}{\partial x_{j>}} \qquad \eta \geq 0 \qquad \text{Navier-Stokes for shear} \tag{4.6}$$

$$\pi = -\nu\frac{\partial v_l}{\partial x_l} \qquad \nu \geq 0 \qquad \text{Navier-Stokes for expansion and compression.} \tag{4.7}$$

This is what we meant earlier when we said that in Eckart's theory the phenomenological laws of Fourier and Navier-Stokes both result from a single and simple thermodynamic argument rather than being separately abstracted from the observed phenomena of heat conduction and internal friction.

Upon close scrutiny of the argument questions do arise about Eckart's simple reasoning. Thus, while it is clear that equations (4.5) through (4.7) are sufficient to guarantee $\sigma \geq 0$, they are not necessary, of course. Few people are worried though. Eckart's simple *derivation* of the laws of Fourier and Navier-Stokes is too suggestive to be questioned much, and the doctrine of proportional fluxes and forces is widely accepted.

With thermal and caloric equations of state $p = p(\rho, T)$ and $u = u(\rho, T)$, and with the constitutive – or phenomenological – equations (4.5) through (4.7) equations of balance (4.1) represent a system of field equations for the determination of $\rho(x_i, t)$, $v_i(x_i, t)$, and $T(x_i, t)$ from initial and boundary values. Every solution is called a *thermodynamic process*. The field equations – being non-linear coupled partial differential equations – are too complicated to be solved analytically in any generality, but solutions for special simple cases fill the textbooks. Usually the problems are made simple by concentrating on *one* field and assuming that the others are zero or constant, whatever the initial and boundary values permit or suggest.

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[28] L/T^2 corresponds to the thermal conductivity κ in (1.1).

4.2.4 Principle of minimal entropy production – a counter example

A particular extremely simple case is stationary one-dimensional heat conduction between two large plates at $x = \pm L$ in a body at rest. That case is really too simple to be considered as such in this report; and yet, just because it is so simple we may use it to exhibit a counter-example to Prigogine's principle of minimal entropy production in a few lines [Barbera 1999]. The energy balance reduces to $\frac{dq}{dx} = 0$ in this case and the Fourier law reads $q = -\kappa(T)\frac{dT}{dx}$; we allow the thermal conductivity to depend on T for generality[29]. For the present simple case we may thus write the only relevant field equation for $T(x)$ in the form

$$\frac{d^2T}{dx^2} + \frac{d\ln\kappa}{dT}\left(\frac{dT}{dx}\right)^2 = 0. \tag{4.8}$$

When the two plates are kept at different temperatures, the temperature field can be obtained from this equation – provided that $\kappa(T)$ is given – and *all is done*: the temperature field is determined by the first law, i.e. the energy equation and *no other criterion is needed*.

And yet, this simple case is the paradigm for the principle of minimal entropy production. I quote Prigogine and Stengers: *the theorem of minimal entropy production shows that a system... tends to a stationary state which is characterised by minimal entropy production, compatible with the boundary constraints, ... for instance when two points are kept at different temperatures* [Prigogine 1983].

This is not so! There is no such theorem! For proof let us consider the entropy production Σ which, in the case under consideration, has the density $\sigma = q\frac{d}{dx}(\frac{1}{T})$, cf. (4.4), and, with $q = -\kappa(T)\frac{dT}{dx}$ as before, we obtain

$$\Sigma = \int\limits_{-L}^{L} \frac{\kappa(T)}{T^2}\left(\frac{dT}{dx}\right)^2 dx.$$

Under the stipulated boundary conditions the field $T(x)$, which minimizes Σ, must satisfy the Euler-Lagrange equation

$$\frac{d^2T}{dx^2} + \frac{d\ln\sqrt{\frac{\kappa}{T^2}}}{dT}\left(\frac{dT}{dx}\right)^2 = 0. \tag{4.9}$$

Comparison with the energy equation (4.8) shows that the equations are different unless κ is proportional to $1/T^2$, which is not a realistic proposition *for any material*. Even in the case of the linear Fourier law – with a constant κ – the two equations (4.8) and (4.9) are different[30].

It follows that the principle of minimal entropy production as formulated by Prigogine and Stengers[31] contradicts the first law of thermodynamics! So, the principle is not true. However, to many people, it seems to have a certain plausibility, – some

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[29] In the properly linear case, where κ is independent of T, or if the dependence can be neglected, a special case results, but the main argument and the conclusion of this paragraph are unchanged.

[30] The contradiction was demonstrated by Barbera, who also considered viscous friction with an analogous result [Barbera 1999].

[31] See also [Glansdorff 1971]. That book muddles the issue further by minimizing a *weighed entropy production* which, if the truth were known, is quite different from the entropy production itself.

feeling along the line that the earth is flat – and this will guarantee its survival. And Prigogine, its author? Well, one of the authors of this report (I.M.) has heard Prigogine say in 1973 at a professional meeting that the principle of minimal entropy production was *an error*. This moment of truth, however, was short-lived and it did not prevent him and Ms. Stengers from advertising the principle in 1983.

Whatever the future of the principle of minimal entropy production may be, – if it has a future –, it is certain that the Prigogine-Stengers version of it is wrong. There are those who think the principle could perhaps identify uncontrollable boundary data, or other parameters of thermodynamic solutions which cannot otherwise be determined. This may be so; however, proof and demonstrations are needed.

4.3 Mixtures of fluids

Eckart's theory of mixtures of fluids proceeds along the same lines as for single fluids but, of course, there are significant differences in detail, because of the greater complexity of mixtures [Eckart 1940b]. In particular the masses of the constituents are no longer conserved, at least not, if chemical reactions occur.

4.3.1 Equations of balance

The relevant equations of balance for a mixture of ν constituents $(\alpha = 1, 2, \ldots \nu)$ are the equations of balance of masses of the constituents and of momentum and energy of the mixture

$$\frac{d\rho}{dt} + \rho\frac{\partial v_i}{\partial x_i} = 0$$

$$\frac{\partial \rho_\alpha}{\partial t} + \frac{\partial \rho_\alpha v_i^\alpha}{\partial x_i} = \tau_\alpha \quad (\alpha = 1, \ldots \nu)$$

$$\rho\frac{dc_\alpha}{dt} + \frac{\partial J_i^\alpha}{\partial x_i} = \tau_\alpha \quad (\alpha = 1, 2 \ldots \nu - 1)$$

$$\Leftrightarrow$$

$$\frac{\partial \rho v_j}{\partial t} + \frac{\partial \left(\rho v_j v_i - t_{ji}\right)}{\partial x_i} = 0$$

$$\rho\frac{dv_j}{dt} - \frac{\partial t_{ji}}{\partial x_i} = 0$$

$$\frac{\partial \rho\left(u + \frac{1}{2}v^2\right)}{\partial t} + \frac{\partial\left(\rho\left(u+\frac{1}{2}v^2\right)v_i - t_{ji}v_j + q_i\right)}{\partial x_i} = 0$$

$$\rho\frac{du}{dt} + \frac{\partial q_i}{\partial x_i} = t_{ji}\frac{\partial v_j}{\partial x_i}$$

$$(4.10)$$

where c_α are the concentrations of the constituents, τ_α the mass productions, and J_i^α are the diffusion fluxes. The τ_α's are not all independent, because in a chemical reaction the number of atoms of the constituents are conserved; the atoms are just redistributed among the constituents as dictated by the stoichiometric equations. Thus, if γ_α^a are the stoichiometric coefficients of constituent α in reaction a, we have

$$\tau_\alpha = \sum_{a=1}^{n} \gamma_\alpha^a \mu_\alpha \lambda^a. \tag{4.11}$$

n is the number of (independent) reactions, μ_α the molecular mass and λ^a is the reaction rate density.

Equations $(4.10)_1$, or $(4.10)_2$ must be supplemented by constitutive relations for

- the diffusion fluxes J_i^α $(\alpha = 1, 2, \ldots \nu - 1)$;
- the reaction rate densities λ^a $(a = 1, 2 \ldots, n)$;

$$(4.12)$$

- the symmetric tensor t_{ji};
- the flux of internal energy q_i;
- and the specific internal energy u.

4.3.2 Balance of entropy

Again, as in a single fluid, the form of the constitutive relations is motivated by the Gibbs equation. For mixtures this equation, applied to an infinitesimal mass element reads

$$\frac{ds}{dt} = \frac{1}{T}\left(\frac{du}{dt} - \frac{p}{\rho^2}\frac{d\rho}{dt} - g_\alpha \frac{dc_\alpha}{dt}\right). \tag{4.13}$$

where s, u, and p, as well as the chemical potentials g_α are supposed to be functions of ρ, T, and c_α, known from equilibrium thermodynamics. This represents the assumption of local equilibrium in the present case of mixtures.

Elimination of the time derivatives of s, u, and c_α between (4.10) and (4.13) and some rearrangement provides an equation of balance which reads

$$\rho\frac{ds}{dt} + \frac{\partial}{\partial x_i}\left(\frac{q_i - \sum\limits_{\alpha=1}^{\nu} g_\alpha J_i^\alpha}{T}\right) = -\frac{1}{T}\sum_{a=1}^{n}\left(\sum_{\alpha=1}^{\nu} g_\alpha \gamma_\alpha^a \mu_\alpha\right)\lambda^a$$

$$+ q_i\frac{\partial \frac{1}{T}}{\partial x_i} - \sum_{\alpha=1}^{\nu} J_i^\alpha \frac{\partial \frac{g_\alpha}{T}}{\partial x_i} + \frac{1}{T}t_{\langle ij\rangle}\frac{\partial v_{<i}}{\partial x_{j>}} + \frac{1}{T}\left(\frac{1}{3}t_{ii}+p\right)\frac{\partial v_k}{\partial x_k}. \tag{4.14}$$

The equation may be interpreted as an equation of balance of entropy, if we identify

$$\frac{q_i - \sum\limits_{\alpha=1}^{\nu} g_\alpha J_i^\alpha}{T} \quad \text{as the entropy flux, and}$$

$$-\frac{1}{T}\sum_{a=1}^{n}\left(\sum_{\alpha=1}^{\nu} g_\alpha \gamma_\alpha^a \mu_\alpha\right)\lambda^a + q_i\frac{\partial \frac{1}{T}}{\partial x_i} - \sum_{\alpha=1}^{\nu} J_i^\alpha \frac{\partial \frac{g_\alpha}{T}}{\partial x_i} + \frac{1}{T}t_{\langle ij\rangle}\frac{\partial v_{<i}}{\partial x_{j>}} + \frac{1}{T}\left(\frac{1}{3}t_{ii}+p\right)\frac{\partial v_k}{\partial x_k}$$

as the density of entropy production. (4.15)

Inspection shows that the entropy production density is a sum of products, whose factors we may interpret as thermodynamic fluxes and forces as follows

thermodynamic fluxes	and	*thermodynamic forces*
flux of internal energy q_i[32]		temperature gradient $\dfrac{\partial T}{\partial x_i}$
diffusion fluxes J_i^α		chemical potential gradients $\dfrac{\partial\left(-\frac{g_\alpha - g_\nu}{T}\right)}{\partial x_i}$
deviatoric stress $t_{\langle ij\rangle}$		deviatoric velocity gradient $\dfrac{\partial v_{<i}}{\partial x_{j>}}$
dynamic pressure $\pi = -p - \dfrac{1}{3}t_{ii}$		divergence of velocity $\dfrac{\partial v_k}{\partial x_k}$
reaction rate densities λ^a		chemical affinities $\sum\limits_{\alpha=1}^{\nu} g_\alpha \gamma_\alpha^a \mu_\alpha$.

(4.16)

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[32] It is for a good reason that q_i is not called the heat flux at this point, because it contains several additional terms, – additional to the heat flux – which are due to the diffusive motion. We shall come back to this point in Section 5.

4.3.3 Constitutive equations for mixtures

By the second law the entropy production should be non-negative. And this require-
ment may be satisfied in a linear theory by making the fluxes linear homogeneous
functions of the forces.

$$\lambda^a = -\sum_{b=1}^{n} L_{ab} \left(\sum_{\alpha=1}^{\nu} g_\alpha \gamma_\alpha^b \mu_\alpha \right) + L_a \frac{\partial v_k}{\partial x_k}$$

$$\begin{bmatrix} L_{ab} & L_a \\ \tilde{L}_b & \lambda \end{bmatrix} \quad - \text{ non-negative definite}$$

$$\frac{1}{3} t_{ii} + p = -\sum_{b=1}^{n} \tilde{L}_b \left(\sum_{\alpha=1}^{\nu} g_\alpha \gamma_\alpha^b \mu_\alpha \right) + \nu \frac{\partial v_k}{\partial x_k}$$

$$q_i = \kappa T^2 \frac{\partial \frac{1}{T}}{\partial x_i} + \sum_{\beta=1}^{\nu-1} B_\beta \frac{\partial - \left(\frac{g_\beta - g_\nu}{T} \right)}{\partial x_i}$$

$$\begin{bmatrix} \kappa T^2 & B_\beta \\ \tilde{B}_\alpha & B_{\alpha\beta} \end{bmatrix} \quad - \text{ non-negative definite}$$

$$J_i^\alpha = \tilde{B}_\alpha \frac{\partial \frac{1}{T}}{\partial x_i} + \sum_{\beta=1}^{\nu-1} B_{\alpha\beta} \frac{\partial - \left(\frac{g_\beta - g_\nu}{T} \right)}{\partial x_i}$$

$$t_{\langle ij \rangle} = 2\eta \frac{\partial v_{<i}}{\partial x_{j>}}. \tag{4.17}$$

This is a remarkable set of equations. It incorporates all that is known and expected
from irreversible thermodynamics of heat conduction, internal friction, diffusion, and
chemical reaction, albeit for the linear regime. The discussion of the scalar equa-
tions $(4.17)_{1,2}$ which involve chemistry will be postponed to Section 4.3.5. But let
us consider some of the attractive features represented by the vectorial constitutive
equations.

First of all, the terms in (4.17) with κ, η, and ν are already known from single
fluids, where they are the only ones, and they represent the laws of Fourier and Navier-
Stokes of old. Diffusion and the possibility of chemical reactions change the situation
and make the equations more complex.

From $(4.17)_{3,4}$ we may conclude that it is primarily the gradients of the chemical
potentials – not the concentration gradients – that *drive* diffusion. This observation
fits well to the pivotal position of chemical potentials which, like temperature, tend
to become homogeneous fields in equilibrium. Of course, since the chemical potentials
are functions of T, p, and the c_α's, Fick's law (1.6) is not invalidated; it turns out
to represent the special case of isothermal and isobaric diffusion, which is the most
common case.

Moreover, by $(4.17)_{3,4}$, the chemical potential gradients may affect the flux of
internal energy and the temperature gradient may affect the diffusion fluxes. Those
effects are known as the diffusion-thermo effect and thermal diffusion, respectively, and
both are observed, and they are also confirmed by the kinetic theory of gas mixtures.
Thermal diffusion plays a role in the separation of isotopes like U^{238} and U^{235}; it is
routinely relied upon to enhance the separation process in centrifuges.

There are numerous special examples for the usefulness of Eckart's theory. A neat instructive one concerns heat conduction between two parallel plates. The plates are kept at different temperatures and between them we have a mixture of ideal gases, for instance molecular and atomic hydrogen, H_2 and H. By mass action the constituent H will then have a higher concentration near the hot plate than near the cold one. And that difference of concentration and temperature sets up a gradient of chemical potentials which leads to diffusion. de Groot and Mazur include the stationary solution of that process of coupled heat conduction, diffusion and chemical reaction among their exercises [de Groot 1974], see also [Müller 2009].

All of this is good and one might say that Eckart's theory has made irreversible thermodynamics of mixtures accessible to chemists and physicists. It is a popular theory – and not a bad one either – but it is not perfect.

The root cause of the deficiencies lies in the fact that the inertia of the diffusive motion, and hence the kinetic energy of the diffusive motion, are neglected by Eckart. In other words: a proper thermodynamic theory of mixtures should be based on the equations of motion of momenta for all constituents, rather than only on the balance of momentum for the mixture as a whole. We shall come back to this point in the discussion of extended thermodynamics of mixtures (see Sect. 5) which does better in this respect.

Having given Eckart's two articles on irreversible thermodynamics the emphasis which they deserve, we should like to end this section by mentioning that Eckart wrote a third paper in the same year 1940 [Eckart 1940c]. In that paper he derived the relativistic generalisation of Fourier's law

$$q_i = -\kappa \left(\frac{\partial T}{\partial x_i} + \frac{T}{c^2} \dot{v}_i \right).$$

Thus in relativity the heat flux depends on the acceleration $\dot{v}_i$, e.g. the gravitational acceleration, so that the temperature field in a gravitational field is not homogeneous in equilibrium. But there is no room in this report for relativistic irreversible thermodynamics.

4.3.4 Onsager relations for TIP?

We have discussed Onsager relations in Section 3 and we have seen that given the validity of the mean-regression hypothesis (see Sects. 3.2.3 and 3.2.4) such relations can be proved for ordinary differential equations, i.e. rate-type equations of the form (3.2), with relaxation processes of the form (3.3) as solutions. In TIP, however, we deal with transport processes which are governed by partial differential equations. Nothing can be proved concerning Onsager relations in this case, or, if we try, we run into inconclusive results of the type (3.17) discussed in Section 3.5. Nevertheless Meixner has *postulated* symmetry of the matrices listed in (4.17) and, since they were pronounced authoritatively as Onsager relations, they are eagerly accepted by physicists and chemists, whose theories suffer from an overabundance of phenomenological coefficients which are difficult to measure [Meixner 1941; 1943].

However, forces and fluxes are not uniquely defined: if either set is replaced by linear combinations of the forces and fluxes defined in (4.16), the entropy production remains a sum of products but Onsager relations do not in general survive this transformation, even if they have held for the original set. And who is to say that our set (4.16) is the preferred one for which the symmetries do hold? Another subtlety was pointed out by Casimir [Casimir 1945]. He noticed that if some variable is odd under time reversal, for instance the diffusion flux, the symmetry relations involving

that variable become anti-symmetry relations. Both these aspects – transformation of forces and fluxes and odd variables – are discussed at length in the literature, and the book by de Groot and Mazur reflects the discussions in a somewhat confusing manner.

However, in some instances the kinetic theory of gases confirms symmetry relations for diffusion and thermal diffusion. Truesdell has also proved the symmetry of the matrix $B_{\alpha\beta}$, see (4.17), from momentum conservation under the – perhaps – plausible assumption of *binary action* by which the interaction force between two constituents is unaffected by the presence of other constituents, see Section 5 [Truesdell 1968]. In both cases, the kinetic arguments and the concept of binary action, the proofs of symmetry make no use of Onsager's hypothesis of mean regression of fluctuations. This means that there are alternative reasons, valid in specific cases, for a matrix to be symmetric. Most recently Wen-An Yong has discovered a proof of symmetry of force-flux relations in extended thermodynamics of moments which we shall describe in Section 9 [Wen-An Yong 2007].

And what about experimental confirmation? A naïve reader might ask that question, because he does not know that theoreticians seldom dabble in experiments. Experimentation is too difficult for them! However, there is a notable exception: Miller has investigated the validity of Onsager relations experimentally and, in particular, the symmetry of the diffusion matrix in ten ternary mixtures, the simplest conceivable case[33]. He came to the conclusion that in eight out of ten mixtures the symmetry was confirmed – to within experimental error – and in two of them it was not [Miller 1960]. Now, does that mean that Onsager relations are confirmed or refuted? Or does it mean that Truesdell's binary-action-assumption does not hold in the divergent two mixtures? We do not know the answer and we suggest that *a researcher is well-advised not to assume Onsager relations for transport phenomena, at least not, if he wishes to stay on safe ground with his arguments.*

4.3.5 Oscillatory reactions and dissipative structures

Let us now discuss the equations $(4.17)_{1,2}$ which involve chemical reaction densities and affinities. In fact $(4.17)_1$ generalises the phenomenological equations proposed by de Donder for chemical reactions [de Donder 1927]: according to these the rates of reaction are determined by the affinities[34]. However, here there is the possibility that an expansive or compressive motion may lead to chemical reactions even when the affinities vanish. Also, by $(4.17)_2$ chemical affinities may affect the dynamic pressure, even when there is no motion. We do not know whether such effects have ever been observed and we rather think not.

If there is no motion and no chemical reaction, equation $(4.17)_1$ implies the laws of mass action for chemical equilibrium, by which the affinities of all reactions vanish

$$\sum_{\beta=1}^{\nu} g_\beta \gamma_\beta^a \mu_\beta = 0 \qquad (a = 1, 2 \ldots n). \tag{4.18}$$

Otherwise, i.e. if there *are* reactions, the affinity of reaction a may affect the rate of reaction b and vice versa.

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[33] Binary mixtures are uninteresting with regard to Onsager symmetry of the matrix $B_{\alpha\beta}$ of diffusion coefficients, since there is only *one* diffusion coefficient.

[34] de Donder thus gave a modern interpretation of chemical affinities which clarified – and superseded – the old quasi-alchemistic notion conceived by early chemists like Torbern Olof Bergman (1735–1784) or Claude Louis Comte de Berthollet (1748–1822).

It remains for the chemist to find out which are the independent reactions and what their number n is. This involves complex chemical analysis: even the most common overall chemical reactions, such as the formation of water by $2H_2 + O_2 \rightarrow 2H_2O$ or the ammonia synthesis $3H_2 + N_2 \rightarrow 2NH_3$ – need catalysts for intermediate reactions like the dissociation of H_2, O_2, or N_2. Otherwise they are frozen, i.e. suppressed at low temperature, or the reactions proceed only at high pressures. Sometimes more than one chain of reactions may lead to the same results, albeit at different rates. The task of the chemist is not an easy one, and the phenomenological law $(4.17)_1$, while correct, has a very restricted usefulness as a contribution to chemical kinetics. It is deceptive in its simplicity. Feinberg discusses in a fairly mathematical form what is involved and his analysis makes stoichiometry an interesting application of linear algebra [Feinberg 1979].

Another difficulty with the phenomenological equation $(4.17)_1$ – apart from the identification of independent reactions – is the occurrence of the chemical potentials. Even if their dependence on T, p, and c_α^h is known for all constituents $\alpha = 1, 2, \ldots \nu-1$ in all occurring phases $h = 1, 2, \ldots f$ – which is seldom the case – the dependence on c_α^h is very often, or really always, non-linear. Therefore without diffusion the rate laws $(4.10)_1$ provide non-linear ordinary differential equations with an interesting wealth of possible solutions: Apart from innocuous – and expected – simple relaxations to chemical equilibrium there may be *chemical oscillations* like those observed in the Belousov-Zhapotinsky reaction [Belousov 1958; Zhapotinsky 1964].

The Belousov-Zhapotinsky reaction was the first example for a homogeneous chemical oscillation. Belousov observed an oscillatory colour change during an oxidation of citric acid with a bromate solution and cerium as a catalysts. After initial scepticism the chemical community studied the process intensively and came up with up to 20 independent intermediate reactions[35]. We cannot go into such detail in this report.

Anyway, the effect of intermediate catalytic constituents in reactions like the Belousov-Zhapotinsky reaction are too complex to be interpreted in simple words and to be grasped intuitively. Therefore we often fall back on model reactions. Prigogine et al. have invented a fairly simple reaction between two constituents x and y which models an oscillatory reaction like the Belousov-Zhapotinsky one; they call their system of equations the Brusselator [Prigogine 1977][36].

$$\frac{dx}{dt} = x_s + x^2 y - x_s y_s x - x$$

(x_s, y_s) is a stationary composition.   (4.19)

$$\frac{dy}{dt} = x_s y_s x - x^2 y$$

Figure 9 exhibits the graph of a solution for a particular choice of parameters and for particular initial conditions. The solution approaches a *limit cycle* so that the densities of both constituents x and y oscillate. A phenomenon like this may be interpreted as a case where continual dissipation in a body is offset by stationary in- and effluxes of constituents so that stable oscillations may occur in the body indefinitely.

Prigogine's work could take advantage of the earlier work by chemists, in particular Lotka and of the theory of non-linear ordinary differential equations which had been developed by mathematicians like Volterra. Both became famous for their socio-biological model of a predator-prey society [Lotka 1910; Volterra 1931].

[35] For a simplified model reaction and some history see Wikipedia: Belousov-Zhapotinsky reaction.
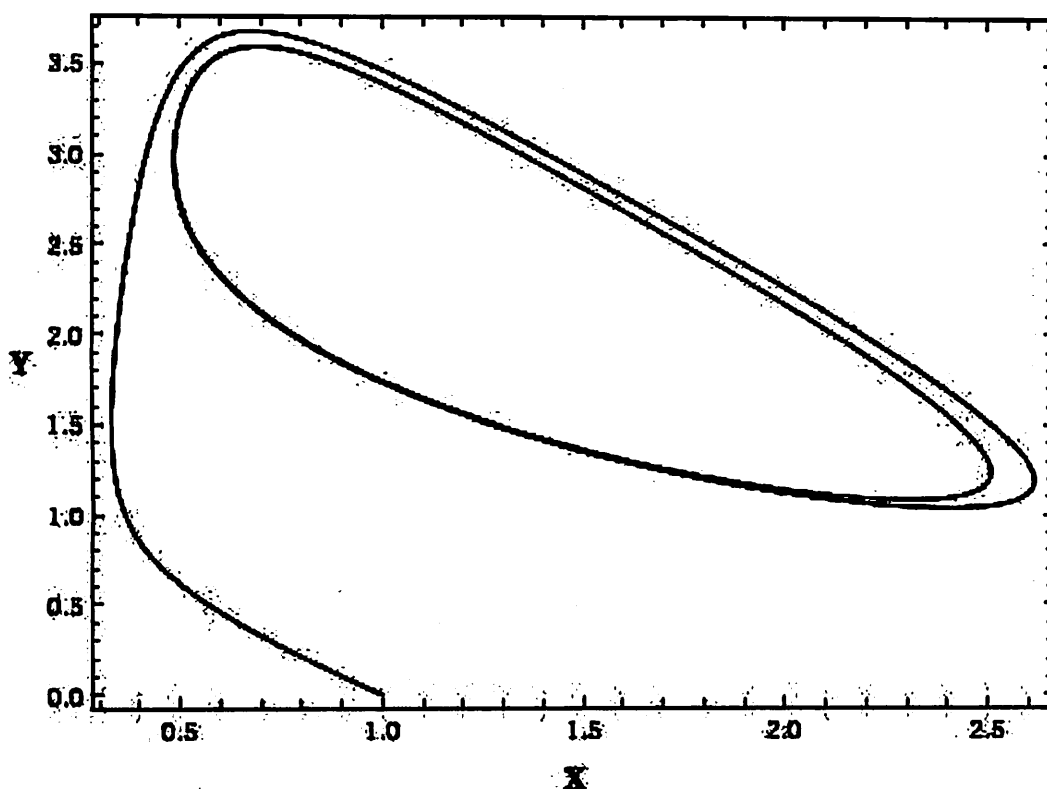[36] x and y in the equations and in the figure stand for the densities of the constituents.

Fig. 9. Limit cycle of the Brusselator[37] $x_s = 1$, $y_s = 2.5$, $x(0) = 1$, $y(0) = 0$.

Prigogine advertised this line of research and made chemists aware of the rich properties of the non-linear differential equations in the field of chemical thermodynamics. His work became quite popular, because it is great fun to plot the solutions-graphs of non-linear systems upon changes of parameters and initial conditions. Thus Prigogine was awarded the Nobel prize for chemistry in 1977.

In order to anticipate a common misunderstanding of the significance of the non-linear differential equations for the constituent densities in a mixture we like to say this: these processes are *not* far from equilibrium. They are all covered by Eckart's equations which are *linear* relations for the chemical potentials. The non-linearity of the differential equations results from the non-linearity of the relations between the chemical potentials and the concentrations[38]. The misunderstanding may be excused, perhaps, because we cannot observe, – i.e. see, hear or smell –, the chemical potentials, and how close they are to equilibrium, while we may be able to determine concentrations by sight through colour changes (say).

If there is diffusion in addition to chemical reactions, equations $(4.10)_1$ remain partial differential equations instead of being reduced to ordinary ones. The solutions may exhibit striped patterns in such cases, or rings, or hexagons. Actually we do not necessarily need chemistry to observe such pattern formation. Even in a layer of a single fluid heated from below we commonly observe convection patterns due to the interaction of thermal conduction and gravity [Bénard 1900]; there are also regular Taylor vortices in a fluid between rotating cylinders due to shearing and inertial forces. Prigogine has introduced the term *dissipative structures* for such phenomena. Each one requires its own physical interpretation and a mathematical analysis of its own.

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[37] The graph of the figure is taken from Wikipedia: Brusselator.

[38] Even in equilibrium most relations between the concentrations in a reacting mixture are non-linear, of course, according to the law of mass action.

5 Rational thermodynamics

5.1 Abstract

In the 1960's TIP was briefly pushed into second place when a more systematic theory was proposed: Rational thermodynamics. But in the end that theory failed in its simplest applications when it turned out that it led to instability for non-Newtonian fluids.

5.2 Clausius-Duhem inequality and material frame indifference

Despite the suggestive character of Eckart's doctrine of forces and fluxes there was room for improvement. Eckart's theory glosses over the question for which fields $\rho(x_j, t)$, $v_i(x_j, t)$, $T(x_j, t)$ the entropy inequality must hold; also it clearly presents itself as a somewhat naive extrapolation of relations from equilibrium thermodynamics, the Gibbs equation (4.2), for instance, or the assumption of local equilibrium, or the relation (4.4)$_1$ between the fluxes of entropy and internal energy.

Therefore the new *rational thermodynamics* – formulated in the 1960's – came up with the requirement that *the Clausius-Duhem inequality* (2.2) *must hold for all solutions of the field equations*, which are composed of the conservation laws of mass, momentum and energy and supplemented by constitutive equations. In this manner the Clausius-Duhem inequality could serve as a constraint on the generality of the constitutive functions, and local equilibrium was no longer needed as an a priori assumption; in some cases it came out as a result. Coleman and Mizel stress that latter point [Coleman 1964].

For reasons to be discussed below the Clausius-Duhem inequality is given an extra term which makes the radiative heating explicit. In local form it reads

$$\rho \frac{ds}{dt} + \frac{\partial \left(\frac{q_i}{T} \right)}{\partial x_i} - \frac{\rho r}{T} \geq 0, \tag{5.1}$$

where ρr is the density of radiative heating, or cooling. The additional radiative term makes sense in terms of Clausius's formulation of the second law, see Section 2.2, and it is needed for the mathematical consistency of rational thermodynamics.

In order to avoid misunderstanding we must say, that the Clausius-Duhem inequality (5.1) does not account for the physics of the interaction of matter and radiation, because s is the entropy of the matter only and q_i/T is the entropy flux of the matter. Entropy and entropy flux of radiation are not considered here. We do not elaborate this point; the interested reader is referred to some articles by Weiss on the entropy of the earth [Weiss 1996a; 1998].

Rational thermodynamics made full use of the principle of material frame indifference of continuum mechanics, by which the constitutive functions must be free of inertial terms due to Coriolis forces, or centrifugal forces and such like [Noll 1958]. Much of Eckart's linear force-flux relations are implied by that principle alone, and all that remains for thermodynamics to do is confirmation of the inequalities for transport coefficients, like the viscosities, or the thermal conductivity.

Both are attractive – and welcome – features in thermodynamics, and so Truesdell advertised rational thermodynamics with some verve, hailing the theory as the true beginning of non-equilibrium thermodynamics [Truesdell 1966; 1969]. It was he who dubbed the theory *rational thermodynamics*; the implied derogatory slant on earlier theories was fully intended, although never openly admitted.

5.3 The roles of radiation and gravitation

Naturally, such exaggerated praise provoked a reaction among the people who had laboured in the field all their lives. Meixner tried to be conciliatory in his paper *TIP has many faces* [Meixner 1968]; to no avail, because to Truesdell TIP was a dirty word. And then there was Woods, Leslie Colin Woods of Oxford, applied mathematician and former fighter pilot – according to his vita in the Internet. In the true spirit of combat he published a provocative paper entitled *The bogus axioms of continuum mechanics* [Woods 1981]. Woods had many complaints about rational thermodynamics and continuum mechanics – eight of them, some quite justified – but what infuriated him most was the role of radiation r and gravitation f_i in the exploitation of the Clausius-Duhem inequality (5.1). That feature deserves a comment.

Coleman and Noll, the main proponents of rational thermodynamics wrote the equations of balance of momentum and internal energy in the forms [Coleman 1963; 1964]

$$\rho\frac{dv_j}{dt} - \frac{\partial t_{ji}}{\partial x_i} = \rho f_j \quad\text{and}\quad \rho\frac{du}{dt} + \frac{\partial q_i}{\partial x_i} = t_{ij}\frac{\partial v_i}{\partial x_j} + \rho r. \tag{5.2}$$

They considered the gravitational body force f_i and the radiation supply r as potentially arbitrarily adjustable fields so that the solutions $\rho(x_j,t)$, $v_i(x_j,t)$, $T(x_j,t)$ of the field equations are not restricted by the balance equations (5.2) when the Clausius-Duhem inequality is exploited. This stratagem may have been acceptable to mathematicians, but to physicists it was absurd. Woods called it the phlogiston principle[39] and had his fun with it. The title of Woods's *bogus*-paper and its style is typical for the tone of the argument that was carried on about rational thermodynamics. Rivlin happily joined the fray with sarcastic lectures to a world-wide audience: *On red herrings and other sundry unidentified fish in modern continuum mechanics.*

5.4 Improvements

All the polemics, however, did not do any damage to the popularity of rational thermodynamics. Quite the contrary: the theory thrived and grew and dominated the thermodynamic literature for a decade after it was conceived. It was improved too: thus Müller avoided Woods's phlogiston-objection by taking the balance equations of momentum and energy into account explicitly in the evaluation of the entropy inequality – without radiative and gravitational terms [Müller 1970]. Liu then streamlined that approach by the introduction of Lagrange multipliers [Liu 1972a; 1972b]. Again Müller allowed the entropy flux to be a constitutive quantity in its own right, a priori unrelated to the heat flux [Müller 1967a; 1967b]. Such improvements were later made essential parts of extended thermodynamics, see Sections 8 and 9.

5.5 Instability

Despite such efforts rational thermodynamics failed in the end when it turned out that for non-Newtonian fluids it leads to instability. Let us explain that aspect suggestively, cutting away unessential formalism and superficial complication.

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[39] The phlogiston was the hypothetical weightless substance, which scientists up to the late 18th century believed was responsible for heating and corrosion. It is difficult to see a connection to Woods's objection.

Rheology had made impressive progress in the 1950's in treating visco-elastic fluids, so-called non-Newtonian fluids. Those fluids have a memory and their deviatoric stress $t_{\langle ij \rangle}$ at time t depends on the present value *and* the past history of the shear rate $\frac{\partial v_{<i}}{\partial x_{j>}}$. In a simple case, using a Taylor expansion of the history at the present time, one may be tempted to write

$$t_{\langle ij \rangle} = 2\eta \left(\frac{\partial v_{<i}}{\partial x_{j>}} - \tau \frac{d}{dt} \frac{\partial v_{<i}}{\partial x_{j>}} \right), \tag{5.3}$$

where, naturally, τ is positive, since it characterises a time in the past. That is – in a nutshell – what rational thermodynamics starts with[40]. But the equation (5.3) is deeply flawed: Indeed, for $t_{\langle ij \rangle} = 0$ it predicts an exponential growth of the shear rate when, instead, we confidently expect the shear rate to decay[41].

This type of instability was discovered in rational thermodynamics of non-Newtonian fluids by Dunn and Fosdick [Dunn 1974][42]. To be sure, their paper was encumbered with considerable formalism, and was therefore not easily appreciated. In fact, at the beginning the disaster was considered as an isolated incidence that might not really bring the theory down. But then came Joseph who drove the final nail into the coffin with his paper: *Instability of the rest state of fluids of arbitrary grade greater than one* [Joseph 1981]. He showed that non-stationary solutions of the field equations based on (5.3) – or on more elaborate expansions – all blow up.

After that rational thermodynamics faded away. The burial was not greeted with the same fanfare that had hailed its emergence, not even by Woods. The occasion was not advertised, and so we may assume that Woods never heard about it. Rather the main contributors went off to investigate other subjects and it became still around rational thermodynamics. Quietly most people returned to Eckart's theory with all its limitations and resigned themselves to the impression that non-Newtonian fluids will forever remain outside the realm of thermodynamics. And indeed, to this day there is no convincing systematic thermodynamic theory of non-Newtonian fluids, although extended thermodynamics seems to point in the right direction, see Sections 8 and 9, and the Outlook in Section 10.

5.6 Lessons

Rational thermodynamics had enriched thermodynamics with some good arguments and a clarification of the underlying principles. Above all there was the proper emphasis on the restrictive role that the entropy inequality plays on the form of the constitutive functions. And there was the clear statement that the entropy inequality has to hold for all thermodynamic processes, i.e. solutions of the field equations. In addition, rational thermodynamics provided the motivation for the modification of the Clausius-Duhem inequality into a true entropy inequality by making the entropy

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[40] To be sure the principle of material frame indifference does not allow $\frac{d}{dt} \frac{\partial v_{<i}}{\partial x_{j>}}$ to be an additive term in the stress. It requires a properly objective tensor in that place to represent the history of the deformation gradient. An attractive choice for that tensor is the Rivlin-Ericksen tensor of grade 2. And that is what Dunn and Fosdick chose. For the present simplified argument the difference is unessential.

[41] *Mutatis mutandis* this is the same argument which Cattaneo first used for the heat flux and the temperature gradient, see equations (P.1), (P.2) in the Preview.

[42] In the paper of Dunn and Fosdick the instability exhibits itself as a free energy function which has a maximum in equilibrium, when everybody knows that it ought to have a minimum, see Section 2. The wrong behaviour is a direct consequence of the expansion (5.3).
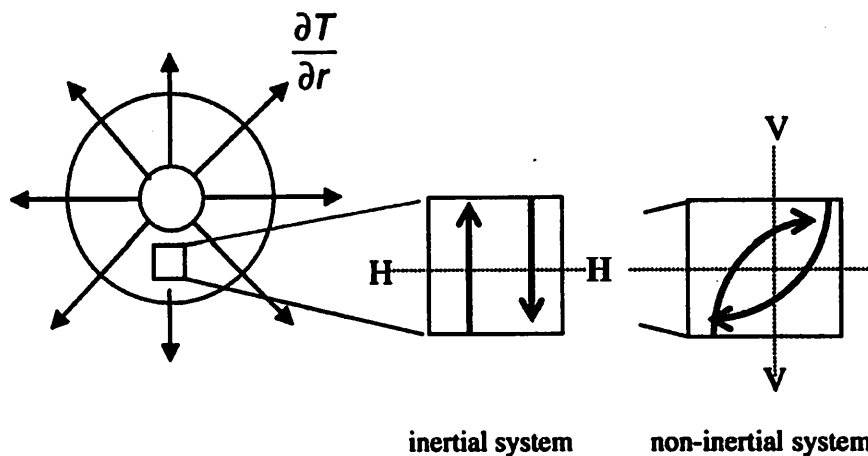
$$\frac{\partial T}{\partial r}$$

inertial system   non-inertial system

Fig. 10. On heat conduction in a non-inertial frame.

flux a constitutive quantity in its own right, a priori unrelated to the heat flux. And then there were Lagrange multipliers for the exploitation of the entropy inequality.

It had not been the entropy principle that failed. Rather it was the constitutive theory with it's claim to represent the past history of $\frac{\partial v_{\leq i}}{\partial x_{j>}}$ by time-derivatives of $\frac{\partial v_{\leq i}}{\partial x_{j>}}$, or by Rivlin-Ericksen tensors at the present time, much as that claim seems plausible. Once this was recognised, the way was free for extended thermodynamics, cf. Sections 8 and 9. That theory was strongly motivated by the kinetic theory of monatomic ideal gases and – in a manner of speaking – it addresses the *non-Newtonian character of ideal gases*. Also, extended thermodynamics lifts Lagrange multipliers up from merely auxiliary fields to an important privileged choice of fields for which the field equations are symmetric hyperbolic. More about this later.

5.7 Limitations of material frame indifference

Whereas the implied instability of non-Newtonian fluids was fatal for rational thermodynamics, the theory had been shaken before, when it turned out that the principle of material frame indifference was wrong [Müller 1972]. Let us consider that argument: Material frame indifference under Euclidean transformations[43] is important for rational thermodynamics, because it forces constitutive functions to be isotropic, and thus it replaces the force-flux strategy of Eckart's theory, cf. Sections 4.2 and 4.3. The principle is therefore an important ingredient of elasticity, rheology, and thermodynamics. But frame indifference is not strictly true; it fails for rarefied gases.

A good simple argument for illustrating this fact starts with the atomistic interpretation of heat conduction which was presented in Section 1.3.

We must first recall the argument around Figure 2, where we showed – on the basis of the atomistic motion in a gas with a temperature gradient – that the flux is proportional to the temperature gradient and opposite to it. Thus Fourier's law was confirmed. The tacit assumption on that previous occasion was that the gas is at rest in an inertial frame. Now we modify the argument by placing the cylinders of Figure 2 on a carrousel which rotates with the angular velocity ω_i with respect to an inertial frame around the axes of the cylinders. In that case the atoms flying inwards and outwards are both forced on circular paths by the Coriolis force, cf. Figure 10. A pair of atoms – one flying inwards and one outwards – will now still carry energy through

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[43] Euclidean transformation are time-dependent rotations and translations.

the horizontal plane H-H, but there will also be an energy transport through the vertical plane V-V, perpendicular to both the angular velocity and the temperature gradient

$$q_i = -\kappa \left(\frac{\partial T}{\partial x_i} + \tau \varepsilon_{ijk} \omega_j \frac{\partial T}{\partial x_k} \right).$$

(5.4)

Thus Fourier's law acquires an additional term which is orthogonal to the temperature gradient and depends on ω_i, the angular velocity *of the frame*. Thus frame *indifference* is violated.

The formal kinetic theory based on the Boltzmann equation makes this illustrative argument more complex and more convincing. What is more: it is not only the heat flux – as in (5.4) – whose relation to the temperature gradient depends on the frame. The stress too, in its relation to the velocity gradient depends on the frame.

It must be admitted, however, that the effect is quite small in most circumstances, because it depends on the extent to which the Coriolis force is able to impart a curvature on the mean free path of the atoms. Another way of saying this is that the frame- dependent term is of the order of magnitude of the mean time of free flight of an atom divided by the period of rotation of the frame. For practical purposes that period cannot be made arbitrarily small.

So, we may say that the principle of material frame indifference is *nearly correct* under all but the most extraordinary circumstances. But this was not good enough for Truesdell. Approximate principles did not exist for him and he responded with a polemic and provocative paper: *Correction of two errors*[44] *in the kinetic theory that have been used to cast unfounded doubt upon the principle of material frame indifference* [Truesdell 1976]. So great were Truesdell's powers of persuasion that it took 30 years until the truth about frame indifference was accepted. The truth is that material frame indifference *does* hold for Galilean transformations, where $\omega_i = 0$ holds, and it is approximately true for Euclidean transformations to the extent described above.

6 Extended thermodynamics of mixtures of fluids

6.1 Abstract

Eckart's theory of mixtures, described in Section 4 is flawed by the neglect of the acceleration of the diffusive motion. Truesdell has corrected the theory in a systematic manner. His arguments provide explicit information about the contributions of diffusion to the stress, the internal energy and the flux of internal energy of the mixture. The latter is split – in a plausible manner – into a heat flux and a flux of internal energy due to the diffusive motion. On this basis an extended theory of mixtures was developed which provides each constituent with its own momentum balance, complete with accelerations, partial stresses, and interaction forces.

Due to the inertia of the diffusive motion there are *two* longitudinal sound modes in extended thermodynamics of binary mixtures. In general these modes are coupled but for particular mixtures they uncouple. If they do, the first sound propagates as a density wave, and the second sound propagates as a concentration wave. The latter is strongly damped and therefore it is never seen, – or heard (!) – under normal circumstances. In liquid helium, however, a *mixture* of a normal fluid and a superfluid, the sounds are uncoupled, and both may be observed, but the second sound can still

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[44] One of the *errors* in Truesdell's opinion was supposed to occur in Müller's argument [Müller 1972], see above. The other one was suspected by Truesdell to be contained in a paper by Edelen and McLennan [Edelen 1973].

not be *heard*, because it degenerates into a temperature wave due to the special low-temperature properties of helium.

Flames and detonations provide a non-trivial application for Eckart's theory and extended thermodynamics of mixtures and allow us to compare their predictions. They are close for the two theories, at least under normal pressures and temperatures.

6.2 Metaphysical principles

Truesdell considers homogeneous mixtures of ν constituents $\alpha = 1, 2, \ldots \nu$ such that all points of the mixture are occupied by molecules of all constituents [Truesdell 1968]. At the outset he postulates equations of balance for the masses, momenta and energies of the constituents of the form

$$\frac{\partial \rho_\alpha}{\partial t} + \frac{\partial \rho_\alpha v_i^\alpha}{\partial x_i} = \tau_\alpha$$

$$\frac{\partial \rho_\alpha v_j^\alpha}{\partial t} + \frac{\partial \rho_\alpha v_i^\alpha v_j^\alpha - t_{ij}^\alpha}{\partial x_i} = m_j^\alpha \qquad (\alpha = 1, 2, \ldots \nu)$$

$$\frac{\partial \rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} v_\alpha^2\right)}{\partial t} + \frac{\partial \left(\rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} v_\alpha^2\right) v_i^\alpha - t_{ji}^\alpha v_j^\alpha + q_i^\alpha\right)}{\partial x_i} = e_\alpha. \qquad (6.1)$$

These equations have the same forms as the conservation laws of a single body except for the production terms τ_α, m_i^α, e_α on the right hand sides which represent the productions of mass, momentum, and energy of the constituents due to their chemical, dynamic, and energetic interactions respectively. In order for mass, momentum and energy *of the mixture* to be conserved, we must require

$$\sum_{\alpha=1}^{\nu} \tau_\alpha = 0 \qquad \sum_{\alpha=1}^{\nu} m_i^\alpha = 0 \qquad \sum_{\alpha=1}^{\nu} e_\alpha = 0. \qquad (6.2)$$

Furthermore Truesdell postulates that the mixture as a whole has conservation laws of the same form as a single body, viz.

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_i}{\partial x_i} = 0$$

$$\frac{\partial \rho v_j}{\partial t} + \frac{\partial \rho v_i v_j - t_{ij}}{\partial x_i} = 0$$

$$\frac{\partial \rho \left(\varepsilon + \frac{1}{2} v^2\right)}{\partial t} + \frac{\partial \left(\rho \left(\varepsilon + \frac{1}{2} v^2\right) v_i - t_{ji} v_j + q_i\right)}{\partial x_i} = 0. \qquad (6.3)$$

Rather obviously then, ρ, v_i, t_{ij}, ε and q_i of the mixture must be defined in terms of the partial quantities by the sums

$$\rho = \sum_{\alpha=1}^{\nu} \rho_\alpha \qquad\qquad \rho v_i = \sum_{\alpha=1}^{\nu} \rho_\alpha v_i^\alpha$$

$$t_{ij} = \sum_{\alpha=1}^{\nu} \left(t_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha\right)$$

$$\rho \varepsilon = \sum_{\alpha=1}^{\nu} \rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} u_\alpha^2\right) \qquad q_i = \sum_{\alpha=1}^{\nu} \left(\rho_\alpha \left(\varepsilon_\alpha + \frac{1}{2} u_\alpha^2\right) u_i^\alpha - t_{ij}^\alpha u_j^\alpha + q_i^\alpha\right),$$

$$(6.4)$$

where $u_i^\alpha = v_i^\alpha - v_i$ is the diffusion velocity, the excess of the velocity of constituent α over the velocity of the mixture.

It follows that the stress of the mixture is not just the sum of the stresses of the constituents; in addition it contains the momentum flux of the diffusive motion. Also the density of internal energy of the mixture is the sum of the partial internal energy densities *plus* the density of the kinetic energy of the diffusive motion. And finally, the flux of internal energy of the mixture is the sum of the heat fluxes q_i^α of the constituents and, *in addition*, it contains the convective flux – with the diffusive motion – of the partial internal and kinetic energies, and the power of the partial stresses on the diffusive motion. Such decompositions of the mixture quantities are conceptually important when problems of heat conduction are accompanied by diffusion as is the case in the propagation of detonations and flames.

Truesdell has stirred up the field of irreversible thermodynamics in the 1960's and, generally, the clarity of his contributions, expressed in a flamboyant style, has stimulated the work of his contemporaries. So also in the field of mixtures. He called the assumptions (6.1) through (6.3), that underlie his mixture theory, *metaphysical principles*.

6.3 Balance equations of extended thermodynamics of mixtures of fluids

From equations (6.1) and (6.3) we choose the equations of balance of masses and momenta of the constituents and the energy conservation law of the mixture as the bases for extended thermodynamics of mixtures. Supplemented by appropriate constitutive relations these balance equations provide field equations for ρ_α, v_i^α, and for the temperature T of the mixture[45].

$$\frac{\partial \rho_\alpha}{\partial t} + \frac{\partial \rho_\alpha v_i^\alpha}{\partial x_i} = \tau_\alpha \quad \text{or} \quad \boxed{\begin{array}{l} \dfrac{\partial \rho}{\partial t} + \dfrac{\partial \rho v_i}{\partial x_i} = 0 \\[2mm] \rho\left(\dfrac{\partial c}{\partial t} + v_i \dfrac{\partial c}{\partial x_i}\right) + \dfrac{\partial J_i}{\partial x_i} = \tau_1 \end{array}}$$

$$\frac{\partial \rho_\alpha v_j^\alpha}{\partial t} + \frac{\partial \rho_\alpha v_i^\alpha v_j^\alpha - t_{ij}^\alpha}{\partial x_i} = m_j^\alpha \quad \text{or} \quad \boxed{\begin{array}{l} \dfrac{\partial \rho v_j}{\partial t} + \dfrac{\partial \left(\rho v_j v_i - t_{ij}\right)}{\partial x_i} = 0 \\[2mm] \dfrac{\partial J_j}{\partial t} + \dfrac{\partial J_j v_i}{\partial x_i} - \dfrac{\partial \left(t_{ij}^2 - c t_{ij}\right)}{\partial x_i} + J_i \dfrac{\partial v_j}{\partial x_i} + \dfrac{\partial \frac{J_i J_j}{\rho c}}{\partial x_i} \\[3mm] \qquad\qquad + t_{ij}\dfrac{\partial c}{\partial x_i} = m_j^1 - \tau_1 v_j \end{array}}$$

$$\frac{\partial \rho\left(\varepsilon + \frac{1}{2}v^2\right)}{\partial t} + \frac{\partial\left(\rho\left(\varepsilon + \frac{1}{2}v^2\right)v_i - t_{ji}v_j + q_i\right)}{\partial x_i} = 0. \tag{6.5}$$

Comparison with (4.10) shows that extended thermodynamics of mixtures has extended (sic) the list of Eckart's balance equations by taking the momenta of all constituents into account. This is tantamount to a proper recognition of the inertia of the diffusive motion.

[45] It is possible – and sometimes appropriate – to introduce a separate temperature for all constituents; but this is seldom done because of the difficulty to assign and control partial temperatures

The framed equations in (6.5) represent·the conservation laws of mass and momentum of a *binary* mixture and the balance equations of the partial mass and momentum of constituent 1 in a binary mixture. $J_j = \rho_1 u_j^1$ is the diffusion flux of constituent 1. The equations are put here to make us appreciate that the partial momentum balance, if properly mutilated, represents Fick's law: indeed, the right hand side of the partial momentum balance represents the drag force on constituent 1 and, if that is taken to be proportional to J_j, we recognize Fick's law in the underlined terms. All the other terms – particularly the acceleration of the diffusive motion – are ignored by Fick's theory of diffusion.

The thermodynamic constitutive theory of mixtures of fluids on the basis of the balance equations (6.5) has been worked out by Müller [Müller 1968] and, in a more modern fashion, by Liu and Müller, who use Lagrange multipliers [Liu 1984]. To interested readers a study of the latter article is recommended; it contains the special case of superfluid helium. The article cannot be replayed in the present report, because the arguments are too complex and long. Let it be said, however, that the momentum productions m_i^α contain the drag forces M_i^α on constituent α exerted by the other constituents. We have

$$m_i^\alpha = M_i^\alpha + \tau_\alpha v_i^\alpha.$$

The drag forces M_i^α are primarily due to relative velocities of the constituents so that the leading term of their constitutive relations may be written as

$$M_i^\alpha = \sum_{\beta=1}^{\nu} M_V^{\alpha\beta} \left(v_i^\alpha - v_i^\beta \right).$$

Truesdell has proved that for *binary drags*, i.e. when the force between constituents α and β is not affected by the presence of a third constituent, momentum conservation implies a symmetric matrix of coefficients [Truesdell 1968]. In order to appreciate that result we need to know that Eckart's diffusion law $(4.17)_4$ comes out from (6.5) as a mutilated form of the balance equation $(6.5)_2$ of momenta, namely when the acceleration of the diffusive motion is ignored. And the symmetry of $M_V^{\alpha\beta}$ implies the symmetry of Eckart's coefficient matrix $B_{\alpha\beta}$ which had previously been *assumed* as an Onsager relation, see Section 4.3.4. So, here we have an occasion where a symmetry of constitutive coefficients may not be due to Onsager's mean regression hypothesis. Müller has strengthened Truesdell's result by showing that Eckart's coefficients B_β and $\tilde{B}_\beta$ of thermal diffusion and the diffusion-thermo effect are equal, if there is no *thermal drag*, i.e. if a temperature gradient does not affect the drag forces M_i^α [Müller 1973]. That plausible assumption renders an Onsager relation superfluous in the present case.

6.4 First and second sound

From particle mechanics we all know that inertia and elasticity between them lead to oscillation, and that an excess of damping, *over-damping*, may disguise the effect of inertia and lead to a simple relaxation. In continuum mechanics this is the same with waves, namely sound waves. Now, in extended thermodynamics of mixtures of ν constituents we have ν accelerations, and that means ν inertial contributions; accordingly we have ν modes of propagation or, in a manner of speaking, ν sounds.

Take a binary mixture of two inviscid and non-reacting simple fluids. Müller and Villaggio have arranged the field equations so as to obtain coupled linear wave

equations for the density ρ and the concentration c [Müller.1976]. They read

$$\frac{\partial^2 \rho}{\partial t^2} - \left[g_\rho + \frac{T p_T^2}{\rho^2 \varepsilon_T} \right] \Delta\rho - W \Delta c = 0$$

$$\frac{\partial^2 c}{\partial t^2} - M_V^{11} \frac{\rho}{\rho_1 \rho_2} \frac{\partial c}{\partial t} - \frac{\rho}{\rho_1 \rho_2} \left[g_c + \frac{T}{\varepsilon_T} \left(\frac{p_T^1}{\rho_1} - \frac{p_T^2}{\rho_2} \right)^2 \right] \Delta c - \frac{\rho_1 \rho_2}{\rho^4} W \Delta\rho = 0, \quad (6.6)$$

where the coupling term W is given by $W = p_c - \frac{T}{\varepsilon_T} p_T \left(\frac{p_T^1}{\rho_1} - \frac{p_T^2}{\rho_2} \right)$. The letter g denotes the chemical potential difference of the constituents, and $p_T^\alpha (\alpha = 1, 2)$ stands for $\frac{\partial p^\alpha}{\partial T}$, the derivative of the partial pressure p^α with respect to T. Other terms in the coefficients are analogously defined.

In order to interpret these equations in terms of undergraduate physics we look at the case when $W = 0$ holds[46]. In that case the first equation becomes an ordinary wave equation for the density ρ with a propagation speed V_ρ, the well-known sound speed

$$V_\rho = \sqrt{g_\rho + \frac{T p_T^2}{\rho^2 \varepsilon_T}}, \quad (6.7)$$

and the second equation becomes a telegraph equation describing the propagation of a damped wave for the concentration c with the speed

$$V_c = \sqrt{\frac{\rho}{\rho_1 \rho_2} \left[g_c + \frac{T}{\varepsilon_T} \left(\frac{p_T^1}{\rho_1} - \frac{p_T^2}{\rho_2} \right)^2 \right]}. \quad (6.8)$$

We call these modes of propagation the *first and second sound*, respectively. Both waves are accompanied by a temperature wave.

The second sound is damped by the occurrence of the coefficient M_V^{11} which is usually so big that the first term, viz. $\frac{\partial^2 c}{\partial t^2}$ in $(6.6)_2$ can be neglected; thus we obtain the ordinary parabolic diffusion equation,

$$\frac{\partial c}{\partial t} - \frac{\rho_1^2 \rho_2^2}{\rho^3} \frac{1}{M_V^{11}} V_c^2 \Delta c = 0 \quad (6.9)$$

just as if we had adopted Fick's law. That case may be called *over-damped*, and over-damping is what usually happens, – in air (say) which, after all, is essentially a binary mixture. Thus – fortunately (!) – we hear only *one* sound.

The parabolic equation (6.9) is mathematically identical to Fourier's heat conduction equation (1.2). And since that earlier equation implied infinite speeds – the paradox of heat conduction, see Section 1.2 – the present one implies infinite speeds as well and we might speak of the *paradox of diffusion*. However, the situation is easy to interpret now, easier than in the case of heat conduction: indeed, the paradox is immediately resolved, because the parabolic equation (6.9) is a limiting case of the perfectly hyperbolic system (6.6) with a finite speed for the propagation of disturbances in concentrations namely (6.8).

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[46] This is not an altogether impractical assumption. Indeed, $W = 0$ holds in a mixture of ideal gases which have equal mol masses. However, here we take $W = 0$ for simplicity; if we did not do so, the argument would be slightly more complex, but we should still have two speeds.
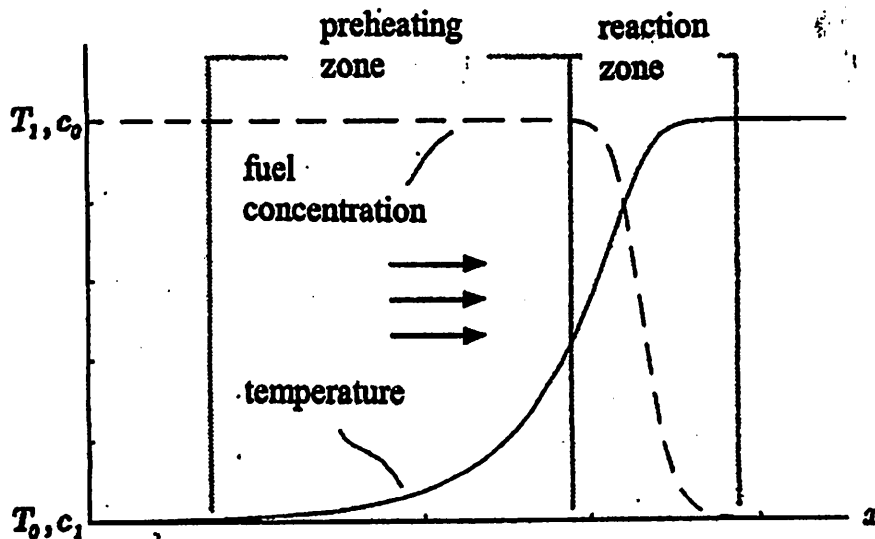
Fig. 11. Schematic view of a flame[48].

The effect of damping diminishes when we go to temperatures close to absolute zero due to quantum mechanical reasons and therefore we can observe *both* sounds in liquid helium below 2.2 K. That remarkable liquid behaves as if it were composed of two constituents, the normal fluid and the super-fluid. If their properties are introduced into the wave equations (6.6) along with $M_V^{11} = 0$, we obtain Landau's equations for liquid helium [Landau 1941], see also [Lifschitz 1944]. They become uncoupled by virtue of incompressibility in that case, i.e. the first sound is not accompanied by a temperature wave, while the second sound is *only* a temperature wave. For a closer description of the case of helium see the article by Liu and Müller cited above. Actually to most physicists the notion of first and second sound refers to liquid helium exclusively. They do not know that both sounds occur in all binary mixtures and that the second sound is merely disguised by damping.

6.5 Detonations and flames. Chapman-Jouguet theory

Non-trivial applications of the theory of mixtures concern detonations and flames. These phenomena exhibit some similarity with shock waves – e.g. sonic booms –, because changes of the thermodynamic fields are confined to a narrow layer. But detonations and flames are richer than shocks, since a chemical reaction occurs inside the layer. We consider a situation in which the reaction zone is stationary, at rest[47], and orthogonal to the x-direction, cf. Figure 11. The onrushing fuel ignites at some temperature and burns in the reaction zone so that the temperature rises there, and the fuel concentration tends to zero. Forward heat conduction into the *pre-heating zone* ensures continued ignition of the newly arriving fuel.

The conservation laws of mass, momentum and energy reduce to the simple form

$$\frac{d\rho v}{dt} = 0, \qquad \frac{d\left(\rho v^2 + p\right)}{dt} = 0, \qquad \frac{d\left(\rho\left(h + \frac{1}{2}v^2\right)v + q\right)}{dt} = 0, \qquad (6.10)$$

[47] Actually we consider a flame (say) which moves uniformly, i.e. with a constant speed. And then we simplify the mathematics by moving with the flame, so that the fuel comes rushing in from the left- hand-side in the figure.

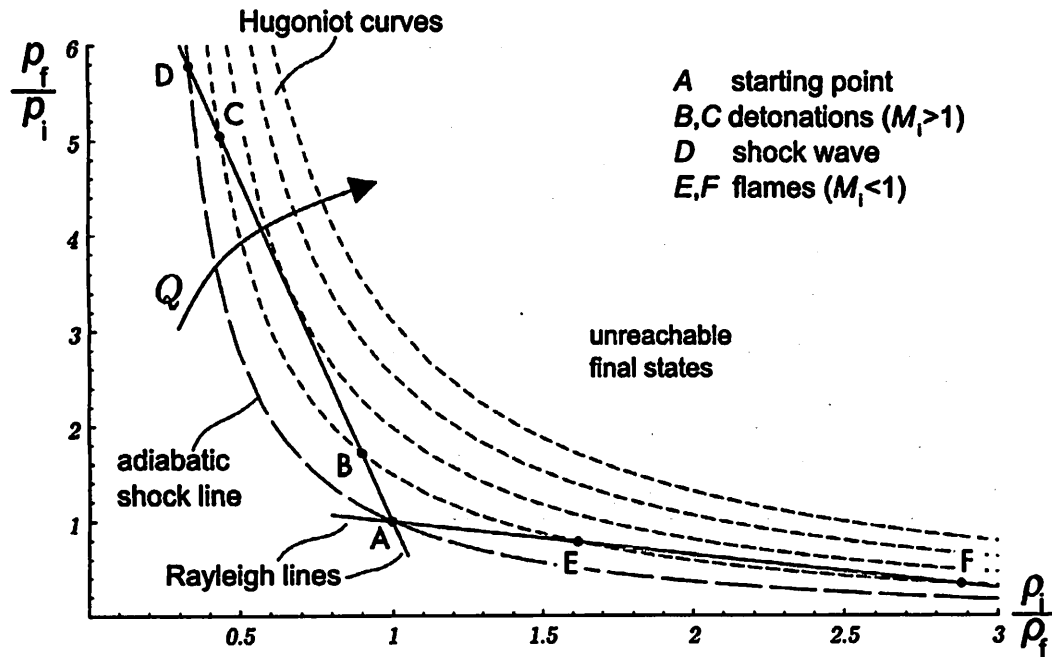[48] The figure is taken from [Torrilhon 1999].

Fig. 12. Hugoniot diagram (for interpretation see text).

when we ignore viscous stresses and introduce the specific enthalpy $h = e + \frac{p}{\rho}$. Also for simplicity we consider the fuel F and the combustion product P as ideal gases with the same mol masses M and specific heats c_p so that $h = h^R + c_p(T - T^R)$ holds with a different h^R for F and P; the difference determines the heat of reaction Q in the reference state R. Equations (6.10) show that the fluxes of mass, momentum and energy are constant throughout the reaction zone. Integration between the initial state i and the final state f — both have $q = 0$, since there is neither heat conduction nor diffusion at those ends — provides two relations for $\frac{p_f}{p_i}$ as a function of $\frac{\rho_i}{\rho_f}$ with the heat of reaction Q and the initial Mach number M_i as parameters, viz.

$$\frac{p_f}{p_i} = 1 + \gamma M_i^2 \left(1 - \frac{\rho_i}{\rho_f} \right), \qquad \frac{p_f}{p_i} \frac{\rho_i}{\rho_f} = 1 + Q + \frac{\gamma - 1}{2\gamma} \left(\frac{\rho_i}{\rho_f} + 1 \right) \left(\frac{p_f}{p_i} - 1 \right). \quad (6.11)$$

These are known as the Chapman-Jouguet relations[49]. Their useful feature lies in the fact that the first one depends only on M_i and the second one on Q[50]. This fact provides us with the possibility of a graphical solution in the Hugoniot diagram of Figure 12 which we proceed to discuss. Instructive representations of the field may be found in [Bartlmä 1975], see also [Hirschfelder 1953].

The initial point is given by $(\frac{\rho_i}{\rho_f}, \frac{p_f}{p_i}) = (1, 1)$ and the solution of $(6.11)_1$ must lie on a straight line through that point, the so-called Rayleigh line. This line is flat for $M_i < 1$ and steep for $M_i > 1$; one each is drawn in the figure. Solutions of $(6.11)_2$ must lie on hyperbolae, so-called Hugoniot curves of which five are drawn in the figure which differ in the heat of reaction Q, including $Q = 0$ which represents the adiabatic shock.

Both equations (6.11) must be satisfied so that p_f and ρ_f can be determined as the coordinates of the points of intersection of the appropriate Rayleigh line and the appropriate Hugoniot curve. Generally there are two points of intersection.

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[49] The presence of the Q-term, the heat of reaction, distinguishes these equations from the Rankine-Hugoniot relations of gas dynamics of shock waves.

[50] γ is the ratio of specific heats, assumed common to both constituents for simplicity.

For the supersonic influx, the case $M_i > 1$, – the steep Rayleigh line –, we speak of a *detonation*. The density grows and the velocity decreases. In Figure 12 possible end-states are denoted by B and C. Note that, as Q tends to zero, the point B eventually coincides with the initial state A, while point C approaches D on the Hugoniot line corresponding to $Q = 0$. This limit state characterises the Rankine-Hugoniot solution behind a shock wave in an inert gas. The shock wave is thus seen as the limiting case of a detonation when no combustion is involved. Here we shall not pursue the case of detonations any further. It is much more difficult than the case of flames. For instance for detonations – as for ordinary shock waves – it is imperative to include the viscosities into the equations. We have never seen that case being developed mathematically.

Therefore we focus on *flames*. These occur for subsonic flow $M_i < 1$, i.e. for the flat Raleigh line. The velocity grows and the density decreases. In the figure the points E and F characterise possible end-states behind the reaction zone.

The natural question whether the flame leads to point E or F does not seem to have a convincing answer in the Chapman-Jouguet theory. People are content with the observation that the flame hardly lowers the pressure and therefore they favour point E. Obviously the entropies ought to differ between the states E and F; so maybe there is room for the principle of minimal entropy production, if anybody could make sense out of that proposition.

6.6 Flame structure

It remains to determine the fields of concentration c, diffusion flux, temperature T etc. inside the reaction zone rather than only their final values. For that purpose we need to integrate the balance equations for the partial masses and partial momenta – as well as the conservation laws for the total mass, momentum and energy, – and that requires the knowledge of the chemical mass consumption τ_1, of the drag force $m_j^1 - \tau_1 v_j$, and of the flux of internal energy $\sum_{\alpha=F}^P q_\alpha$. Reasonable constitutive assumptions for those quantities in the case of a flame are given by

$$\tau_1 = -ac\exp\left(-\frac{E}{kT}\right), \qquad m^1 - \tau_1 v = -p\frac{1}{D}J, \qquad \sum_{\alpha=F}^P q_\alpha = -\kappa\frac{dT}{dx}. \qquad (6.12)$$

a is a material parameter representing the speed of reaction per unit length and E is the activation energy, i.e. the energy needed to ignite the fuel. For the small temperatures in front of the flame the ansatz for τ_1 ensures that τ_1 is very small so that the fuel is in a *frozen* equilibrium. D in $(6.12)_2$ is the diffusion coefficient and κ in $(6.12)_3$ is the thermal conductivity.

Numerical integration of the equations of balance of the partial mass and partial momentum provides the plots of Figure 13 for a reasonable choice of coefficients. The solid curves represent the results of Eckart's theory, while the dashed ones refer to extended thermodynamics of mixtures. For the coefficients chosen here the two theories differ only little. In both cases we observe smooth but steep transitions of c, v, T, and p through the reaction zone, while J has a peak in that zone and is otherwise equal to zero, because two constituents exist only inside the reaction zone.

The numerical integration uses a shooting method from behind the flame to the front, so as to ensure that $c_i \approx 1$ holds[51]. The shooting parameter is the dimensionless flame eigenvalue

$$e = \frac{a}{\rho_i v_i}\frac{\kappa}{c_p\rho_i v_i}, \qquad (6.13)$$

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[51] Au obtains very similar graphs by use of a finite difference scheme [Au 1997].
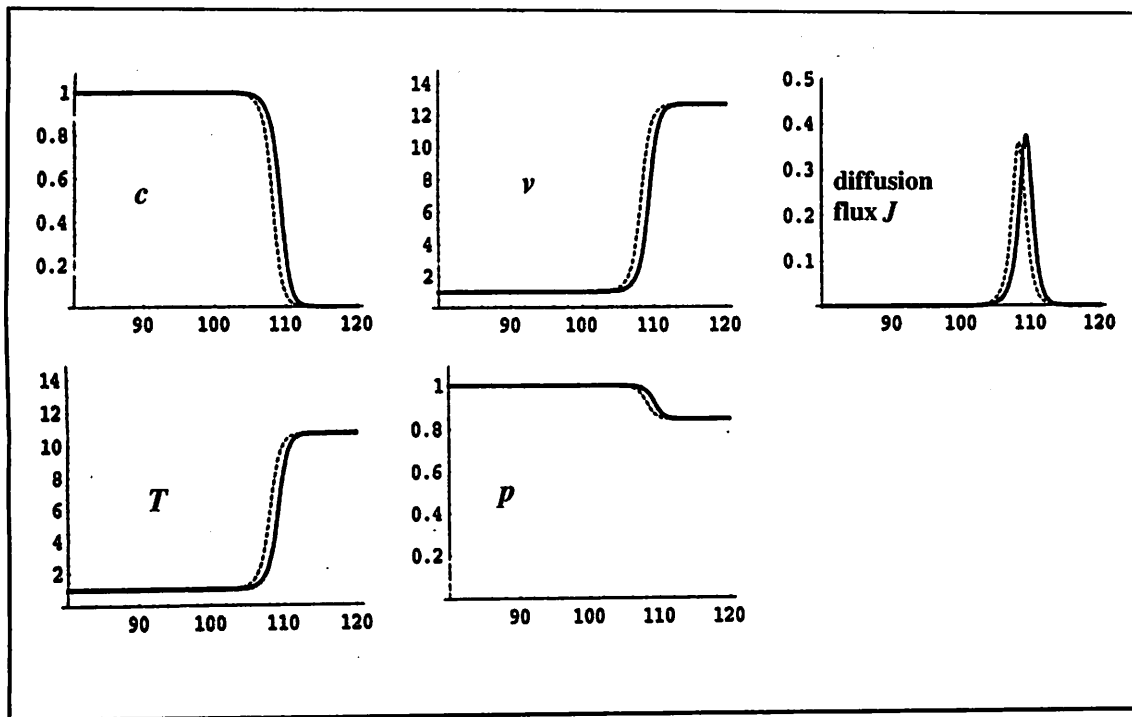
Fig. 13. Flame structure.

whose variation in a very narrow region decides about the existence of a proper solution, i.e. a solution for c that runs from $c \approx 1$ down to $c = 0$. By its definition the flame eigenvalue represents the product of the quotients

- reaction rate over the incoming fuel mass $\frac{a}{\rho_i v_i}$; and
- thermal conductivity over the heat capacity of the incoming fuel $\frac{\kappa}{c_p \rho_i v_i}$.

The sensitivity of the solutions to the eigenvalue e reflects the precariousness of a flame as a physical phenomenon. If e is too large, the flame will be starved of fuel and, if e is too small, the flame will be snuffed out. Also, if κ is small, or if the heat capacity of the incoming fuel is large, the preheating is insufficient for ignition. All these features are combined in the flame eigenvalue.

7 A modicum of the kinetic theory of monatomic gases

7.1 Abstract

Extrapolation is a precarious method of scientific reasoning, and never more so than when we attempt to develop non-equilibrium thermodynamics and have nothing to go by apart from equilibrium thermodynamics. However, we are lucky in thermodynamics, because there is an alternative theory, at least for monatomic gases, that allows us to confirm, or reject, the ad hoc assumptions that have been made in irreversible thermodynamics on the basis of plausibility; a dangerous ground.

Actually the kinetic theory has led to the atomic – or probabilistic – interpretation of entropy that was discussed in Section 2. This constituted enormous progress in natural philosophy, particularly since the interpretation could be extrapolated away from ideal gases; it led to the recognition of the decisive role of stochasticity in nature and of the nature of irreversibility.

Apart from that, the kinetic theory has provided an understanding of the status of material frame indifference, cf. Section 5.7. For that earlier argument a trivial

caricature of the kinetic theory sufficed. This, however, is no longer so when we ask whether or not the kinetic theory confirms Eckart's principle of local equilibrium and the Clausius-Duhem expression for the entropy flux. It does not! Also, what does the kinetic theory have to say about the paradox of heat conduction, see Section 1.2? There is no such paradox in the theory! And what about the classical phenomenological equation, for instance Fourier's law (1.1)? Are they confirmed by the kinetic theory? They are not! Rather they come out as approximations for dense gases.

In order to see all this we need a short account of the formal kinetic theory, based on the Boltzmann equation. Indeed, we dare say that the necessary modifications are such that no amount of creative thinking would have obtained them without the guidance of the kinetic theory.

It turns out that the kinetic theory suggests the balance form for all underlying differential equations, and it provides local and instantaneous constitutive relations. It restricts material frame indifference to Galilean frames and thus has suggested the basic formal structure for extended thermodynamics, which will be the subject of Sections 8 and 9.

7.2 Distribution function, Boltzmann equation, and moments

The kinetic theory of gases describes the state of a gas by the distribution function $f(x_i, c_i, t)$ such that

$$f(x_i, c_i, t)\, dc \tag{7.1}$$

is the number density of the atoms at position x_i and time t which have velocities between c_i and $c_i + dc_i$. The distribution function obeys the Boltzmann equation [Boltzmann 1872], which is a balance equation for the number of atoms in the 6-dimensional phase space spanned by the coordinates x_i and velocities c_i. In modern form this equation reads

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + (g_i + i_i^c) \frac{\partial f}{\partial c_i} = \int \left(f' f^{1'} - f f^1 \right) r V \sin \Theta \, d\Theta \, d\varepsilon \, dc^1. \tag{7.2}$$

where g_i and i_i^c are the gravitational and inertial accelerations of an atom with velocity c_i. Thus

$$i_i^c = \underbrace{2 W_{ik} \left(c_k - \dot{b}_k \right)}_{\text{Coriolis}} - \underbrace{W_{ik}^2 (x_k - b_k)}_{\text{centrifugal}} + \underbrace{\dot{W}_{ik} (x_k - b_k)}_{\text{Euler}} + \underbrace{\ddot{b}_i}_{\text{translation}}, \tag{7.3}$$

where W_{ik} is the matrix of angular velocity of the frame. The right hand side of the Boltzmann equation represents the effect of collisions between the atoms and f, f', f^1, $f^{1'}$ are the values of the distribution function for the velocities c, c', c^1, $c^{1'}$ of two atoms before and after colliding[52]. V is the relative speed of the colliding atoms, r is the cross section for a collision with the parameters ε and Θ.

Most macroscopic thermodynamic quantities in monatomic gases are tensors representing *moments* of the distribution function, viz[53].

$$F_{i_1 i_2 \dots i_N} = \int \mu c_{i_1} c_{i_2} \dots c_{i_N} f \, dc. \tag{7.4}$$

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[52] The form of the collision term on the right hand side of the Boltzmann equation is universally known as the Stoßzahlansatz. The German word has defied translation and is therefore routinely used in English-language texts as well. For its derivation and interpretation one may consult either Boltzmann's article or any book on the kinetic theory, e.g. [Waldmann 1958], or [Chapman 1961].

[53] As always μ is the atomic mass.

Thus, in particular we have

$$\text{mass density} \qquad F = \rho$$
$$\text{momentum density} \qquad F_i = \rho v_i. \tag{7.5}$$

By use of the velocity v_i of the gas we may form the relative – or peculiar – velocity $C_i = c_i - v_i$ of an atom and thus define *internal moments*

$$\rho_{i_1 i_2 \ldots i_N} = \int \mu C_{i_1} C_{i_2} \ldots C_{i_N} f dc. \tag{7.6}$$

Note that ρ_i is equal to zero. The first few moments and internal moments have a canonical notation and are named suggestively

$$F_{ij} - \text{momentum flux} \qquad\qquad -\rho_{ij} = t_{ij} - \text{stress tensor}$$

$$\frac{1}{2} F_{ii} = \rho e - \text{energy density} \qquad \frac{1}{2}\rho_{ii} = \rho u - \text{internal energy density}$$

$$\frac{1}{2} F_{iij} = J_j - \text{energy flux} \qquad \frac{1}{2}\rho_{iij} = q_j - \text{heat flux}. \tag{7.7}$$

In general, i.e. for any tensorial rank, there is a one-to-one relation between the moments and the internal moments of the form

$$F_{i_1 i_2 \ldots i_N} = \binom{N}{0} \rho_{i_1 i_2 \ldots i_N} + \binom{N}{1} \rho_{(i_1 i_2 \ldots i_{N-1}} v_{i_N)} + \binom{N}{2} \rho_{(i_1 i_2 \ldots i_{N-2}} v_{i_{N-1}} v_{i_N)}$$
$$+ \ldots + \binom{N}{N} \rho v_{i_1} v_{i_2} \ldots v_{i_N} \tag{7.8}$$

so that in particular we have

$$F = \rho$$
$$F_i = \rho v_i$$
$$F_{ij} = \rho_{ij} + \rho v_i v_j$$
$$F_{ijk} = \rho_{ijk} + 3\rho_{(ij} v_{k)} + \rho v_i v_j v_k$$
$$F_{ijkl} = \rho_{ijkl} + 4\rho_{(ijk} v_{l)} + 6\rho_{(ij} v_k v_{l)} + \rho v_i v_j v_k v_l. \tag{7.9}$$

In a monatomic gas there is no dynamic pressure. Therefore $-\frac{1}{3}\rho_{ii}$ is equal to the equilibrium pressure p and, by (7.7), we have $p = \frac{2}{3}\rho u$. Thus the thermal or caloric equations of state of a monatomic ideal gas may be used to define temperature

$$p = \frac{\rho}{\mu} kT = \frac{1}{3}\rho_{ii} \qquad \text{or} \qquad u = \frac{3}{2}\frac{k}{\mu} T = \frac{1}{2}\frac{\rho_{ii}}{\rho}. \tag{7.10}$$

The so-defined temperature may be called the *kinetic temperature* because it measures the mean kinetic energy of the atoms.

7.3 Equations of balance for moments

Multiplication of the Boltzmann equation by a generic function $\psi(x_i, c_i, t)$ and integration over all velocities provides a generic equation of balance of the form

$$\frac{\partial \rho\bar{\psi}}{\partial t} + \frac{\partial \overline{\rho\psi c_i}}{\partial x_i} - \overline{\rho(g_i + i_i^c)\frac{\partial \psi}{\partial c_i}} = \overline{\rho\left(\frac{\partial \psi}{\partial t} + c_i\frac{\partial \psi}{\partial x_i}\right)} + \frac{1}{4}\int\left(\psi + \psi^1 - \psi' - \psi^{1'}\right)$$

$$\times \left(f'f^{1'} - ff^1\right) rV\sin\Theta d\Theta d\varepsilon dc^1 dc, \qquad (7.11)$$

where $\bar{\varphi} \equiv \frac{\mu}{\rho}\int \varphi f dc$ defines a mean value. The third term on the left-hand-side represents a supply due to a gravitational force and to inertial forces on atoms with velocity c_i. The integral on the right hand side represents the effect of collisions.

Particularly for $\psi = c_{i_1}c_{i_2}\ldots c_{i_p}$ ($p = 0,1,2,\ldots N$) we obtain balance equations for moments in which the supply term is split into two terms; one due to gravitational forces and inertial forces on the gas with velocity v_i and the other one due to the angular velocity matrix W_{ik} of the frame

$$\frac{\partial F_{i_1\ldots i_p}}{\partial t} + \frac{\partial F_{i_1\ldots i_p n}}{\partial x_n} - pF_{(i_1\ldots i_{p-1}}\left(g_{i_p)} + i_{i_p)}^v\right) - pF_{n(i_1\ldots i_{p-1}}2W_{i_p)n} = \Pi_{i_1\ldots i_p}$$

$$(p = 0,1,2\ldots N). \quad (7.12)$$

The production term on the right hand side of (7.11) is abbreviated by $\Pi_{i_1\ldots i_p}$ here. Its explicit form makes sure that the first five productions, namely Π, Π_i, Π_{ii}, vanish, because the mass, momentum, and energy of the colliding atoms are conserved.

Thus, in particular, the balance equations for the first 20 moments – $F = \rho$, $F_i = \rho v_i$, F_{ij}, F_{ijk} – read

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_n}{\partial x_n} = 0$$

$$\frac{\partial \rho v_i}{\partial t} + \frac{\partial F_{in}}{\partial x_n} - \rho\left(g_i + i_i^v\right) - 2\rho v_k W_{ik} = 0$$

$$\frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijn}}{\partial x_n} - 2\rho v_{(i}\left(g_{j)} + i_{j)}^v\right) - 4F_{n(i}W_{j)n} = \Pi_{ij}$$

$$\frac{\partial F_{ijk}}{\partial t} + \frac{\partial F_{ijkn}}{\partial x_n} - 3F_{(ij}\left(g_{k)} + i_{k)}^v\right) - 6F_{n(ij}W_{k)n} = \Pi_{ijk}. \qquad (7.13)$$

In this explicit form it is obvious that the first two equations represent the conservation laws of mass and momentum. The trace of the third equation represents the conservation law of energy and the remaining 15 equations are equations of balance for the deviatoric momentum flux and for the flux of the momentum flux, both with production terms, viz. $\Pi_{(ij)}$ and Π_{ijk} respectively. In passing we note that all equations, except for the mass balance, contain contributions due to the specific inertial force i_i^v on the fluid, *and* additional inertial contributions due to the rotation of the frame[54].

For some – hypothetical – atoms the dynamics of binary collisions are so simple that the productions can be related to the internal moments explicitly. Thus for

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[54] The inertial contributions to the conservation laws of momentum and energy are ingredients of all classical continuum theories since Euler.

Maxwellian atoms[55] one obtains

$$\Pi_{ij} = -\frac{1}{\tau}\rho_{\langle ij\rangle},$$

$$\Pi_{ijk} = -\frac{1}{\tau}\left(\frac{3}{2}\rho_{ijk} - \frac{1}{6}\left(\rho_{lli}\delta_{jk} + \rho_{llj}\delta_{ik} + \rho_{llk}\delta_{ij}\right) + v_i\rho_{\langle jk\rangle} + v_j\rho_{\langle ik\rangle} + v_k\rho_{\langle ij\rangle}\right). \quad (7.14)$$

Rather obviously τ is a relaxation time for the deviatoric stress and the analysis shows that it is of the order of magnitude of the mean time of free flight of the atoms.

The system (7.13) is typical for the balance laws of a monatomic gas, and the decompositions (7.8), or (7.9) of the moments $F_{i_1 i_2...i_l}$ into internal moments $\rho_{i_1 i_2...i_n}$ ($n \leq l$) turns out to be necessary and sufficient for the balance laws to be valid in all Euclidean frames, inertial or non-inertial [Müller 1993 Chap. 2; 1998 Chap. 4]. In particular, of course, the system is then valid in all Galilean frames, where i_i^v and W_{ij} vanish.

Note that upon first sight the system (7.13) with the productions (7.14) appears to be a system of equations for the 20 moments ρ, v_i, F_{ij}, F_{ijk}. However the system is not closed, because of the appearance of the higher moment F_{ijkn} in (7.13)$_4$, the last flux. Nor does it help to proceed to an equation for the higher moment, because its flux term will bring a moment of the next higher order into the system. This observation represents the *closure problem* of the kinetic theory, and we shall come back to it, cf. Section 7.7.

7.4 Balance of entropy

If we insert

$$\psi = -k\left(\ln\frac{f}{y} - 1\right) \quad (7.15)$$

into the generic equation of balance (7.11), we obtain the equation

$$\frac{\partial\left(-k\int\left(\ln\frac{f}{y} - 1\right)f\,dc\right)}{\partial t} + \frac{\partial\left(-k\int c_i\left(\ln\frac{f}{y} - 1\right)f\,dc\right)}{\partial x_i} = \frac{k}{4}\int\ln\frac{f'f^{1'}}{ff^1}\left(f'f^{1'} - ff^1\right)$$

$$\times rV\sin\Theta\,d\Theta\,d\varepsilon\,dc^1\,dc, \quad (7.16)$$

whose right hand side is obviously non-negative. That observation suggests that we may interpret the equation as an entropy balance with

specific entropy $s = -\dfrac{k}{\rho}\int\left(\ln\dfrac{f}{y} - 1\right)f\,dc$

non-convective entropy flux[56] $\varphi_i = -k\int C_i\left(\ln\dfrac{f}{y} - 1\right)f\,dc$

density of entropy production $\dfrac{k}{4}\int\ln\dfrac{f'f^{1'}}{ff^1}\left(f'f^{1'} - ff^1\right)rV\sin\Theta\,d\Theta\,d\varepsilon\,dc^1\,dc.$

$$(7.17)$$

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[55] These are atoms with a hypothetical repulsive power potential that falls off with the inverse fourth power of the distance of the atoms. It is thought that such an interaction model, while not perfect, is not bad for rarefied monatomic gases.

[56] The total entropy flux is equal to $\rho s v_i + \varphi_i$.

This suggestion is confirmed by the observation that the production term vanishes for the Maxwellian distribution function – the equilibrium distribution of statistical mechanics –

$$f_E = \frac{\rho}{\mu} \frac{1}{\sqrt{2\pi\frac{k}{\mu}T}^3} \exp\left(-\frac{\mu(c-v)^2}{2kT}\right).$$ (7.18)

Indeed, for that equilibrium distribution $(7.17)_1$ assumes the form

$$s_E = \frac{k}{\mu}\left(\ln\frac{T^{3/2}}{\rho} - \ln\left[\frac{1}{\mu}\left(\frac{h}{\sqrt{2\pi k\mu}}\right)^3\right] + \frac{5}{2}\right),$$ (7.19)

which represents the specific entropy[57].

Historically the expression $(7.17)_1$ was the first interpretation of the entropy in term of the distribution of atoms. It was only later – even much later – that the statistical definition (2.7), (2.8) of entropy was arrived at by several ingenious steps of extrapolation including the quantisation of space by de Broglie-type boxes, cf.[58] Section 2. The statistical definition (2.7) has the big advantage, of course, that it is not restricted to monatomic gases. It is true that we have exploited (2.7) only for gases in this article, but the scope of that formula is much wider. It extends to liquids, solids, and polymers, and even to populations of cells and animals, e.g. see [Müller 2010].

7.5 Grad distributions

Harold Grad has proposed to expand the distribution function into a series of Hermite polynomials in terms of the relative velocities C_i [Grad 1949; 1958]. His ansatz reads

$$f = f_E\left(a - a_i\frac{1}{\frac{k}{\mu}T}C_i + a_{ij}\frac{1}{\left(\frac{k}{\mu}T\right)^2}\left(C_iC_j - \frac{k}{\mu}T\delta_{ij}\right)\right.$$
$$\left. - a_{ijk}\frac{1}{\left(\frac{k}{\mu}T\right)^3}\left(C_iC_jC_k - \frac{k}{\mu}T\left(\delta_{ij}C_k + \delta_{kj}C_i + \delta_{ik}C_j\right)\right) + \dots\right).$$ (7.20)

The coefficients $a_{ij\dots l}$ determine to what extent non-equilibrium prevails and, obviously, all coefficients are related to relative moments of the distribution function. We have

$$a = 1, \quad a_i = 0, \quad a_{ij} = \frac{1}{2\rho}\rho_{\langle ij\rangle}, \quad a_{ijk} = -\frac{1}{6\rho}\left(\rho_{\langle ijk\rangle} + \frac{1}{5}\left(\rho_{ill}\delta_{jk} + \rho_{jll}\delta_{ik} + \rho_{kll}\delta_{ij}\right)\right).$$ (7.21)

---

[57] There are subtle differences in the additive constants between this expression for the entropy and previous ones of Section 2. See the footnote in Section 2 concerning (2.11). The present form is the correct one; it represents the classical limit of a proper quantum mechanical calculation of entropy.

[58] When Boltzmann identified the entropy in terms of the distribution function by the expression $(7.17)_1$, it was not done in a systematic manner. Rather in the literature of the time – and in Boltzmann's own writings – the impression is forced upon us that the discovery was a piece of luck, originally not fully understood, or at least not correctly. Afterwards, of course, the kinetic entropy definition was extrapolated into the probabilistic interpretation of the entropy and the lucky find was thus converted into one of the most important and most subtle concepts of physics. The extrapolatory steps are explained in detail and their limitations are pointed out by Müller [Müller 2007].

These are 20 coefficients and, accordingly, the distribution function (7.20) – without higher terms like those with a_{ijkl}, a_{ijklm} etc. – is called the 20-moment Grad distribution. It contains $\rho_{\langle ijk \rangle}$, an internal moment without a suggestive physical interpretation, and therefore Grad has focused his attention on only 13 moments, setting $\rho_{\langle ijk \rangle}$ equal to zero.

We recall (7.7) and arrive at

$$f^{13} = f_E \left(1 - \frac{1}{2p} t_{\langle ij \rangle} \left(\frac{C_i C_j}{\frac{k}{\mu}T} - \delta_{ij} \right) - \frac{1}{p} \frac{q_i C_i}{\frac{k}{\mu}T} \left(1 - \frac{1}{5} \frac{C^2}{\frac{k}{\mu}T} \right) \right) \qquad (7.22)$$

which is known as the 13-moment Grad distribution. It is popular, because all eight coefficients have a suggestive interpretation, namely as deviatoric stress and as heat flux.

7.6 Remark on Chapman-Enskog approximation

More popular – to this day – than the Grad approximation is an earlier attempt by Enskog to approximate the distribution function [Enskog 1917]. This is generally known as the Chapman-Enskog method. In the first iterative step the method recovers the laws of Fourier and Navier-Stokes and it permits the calculation of the transport coefficients, i.e. thermal conductivity and viscosity from an assumed atomic interaction potential. That is good! Further iterative steps in the Enskog scheme are known as Burnett approximation and super Burnett, see [Chapman 1936; 1961], and those are deeply flawed, because they imply instability of non-stationary solutions.

Indeed, if we drop all non-essential terms from the second iterate of the heat flux in the Enskog scheme, we obtain

$$q_i = -\kappa \left(\frac{\partial T}{\partial x_i} - \tau \frac{d}{dt} \frac{\partial T}{\partial x_i} \right) \qquad \text{with} \qquad \kappa, \tau > 0. \qquad (7.23)$$

Therefore the temperature gradient grows exponentially when q_i vanishes, which makes no sense. This is the same type of instability that has already brought down rational thermodynamics – see Section 5.5 – and it is just as deadly for the Chapman-Enskog method which, however, enjoys great popularity to this day. Also we recall that Cattaneo's argument for the resolution of the paradox of heat conduction touched on equation (7.23); see equation (P.1) in the Preview.

Struchtrup has clearly pointed out the instability of the Chapman-Enskog scheme for the case of sound propagation when *all* terms in q_i are considered, rather than only the essential ones which we preserved in (7.23) in order to abbreviate the argument [Struchtrup 2005].

The Grad approximation does better with respect to stability; therefore it is to be preferred.

7.7 Field equations for 20 moments and subsystems

The field equations for the first 20 moments $F = \rho$, $F_i = \rho v_i$, F_{ij}, F_{ijk} are given by the system (7.13). The system may be closed by insertion of $\Pi_{\langle ij \rangle}$ and Π_{ijk} from (7.14) – valid for Maxwellian atoms – and by replacing F_{ijkn} by its value calculated from the 20-moment Grad distribution, so that the internal moment ρ_{ijkn} reads

$$\rho_{ijkl} = 6\frac{k}{\mu} T \rho_{(ij} \delta_{kl)} - 3\rho \left(\frac{k}{\mu} T \right)^2 \delta_{(ij} \delta_{lk)}. \qquad (7.24)$$

Upper left (Euler fluid):

$$\frac{\partial\rho}{\partial t}+\bar{p}\frac{\partial v_j}{\partial x_j}=0$$

$$\frac{\partial v_i}{\partial t}+\frac{\frac{k}{\mu}\bar{T}}{\bar{p}}\frac{\partial\rho}{\partial x_j}+\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}-\frac{1}{\bar{p}}\frac{\partial t_{\langle ij\rangle}}{\partial x_j}=0$$

$$\frac{\partial\frac{k}{\mu}\bar{T}}{\partial t}+\frac{2}{3}\frac{k}{\mu}\bar{T}\frac{\partial v_k}{\partial x_k}+\frac{2}{3}\frac{1}{\bar{p}}\frac{\partial q_k}{\partial x_k}=0$$

$$\frac{\partial t_{\langle ij\rangle}}{\partial t}-\frac{4}{5}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}-\frac{\partial p_{\langle ijk\rangle}}{\partial x_k}-2\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=-\frac{3}{2}\frac{1}{\tau}t_{\langle ij\rangle}$$

$$\frac{\partial q_i}{\partial t}-\frac{k}{\mu}\bar{T}\frac{\partial t_{\langle ik\rangle}}{\partial x_k}+\frac{5}{2}\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}=-\frac{1}{\tau}q_i$$

$$\frac{\partial p_{\langle ijk\rangle}}{\partial t}-3\frac{k}{\mu}\bar{T}\left(\frac{\partial t_{\langle ij\rangle}}{\partial x_{k\rangle}}-\frac{2}{5}\frac{\partial t_{\langle kl\rangle}}{\partial x_r}\delta_{jk\rangle}\right)=-\frac{9}{4}\frac{1}{\tau}p_{\langle ijk\rangle}$$

Upper right (Navier-Stokes-Fourier fluid):

$$\frac{\partial\rho}{\partial t}+\bar{p}\frac{\partial v_j}{\partial x_j}=0$$

$$\frac{\partial v_i}{\partial t}+\frac{\frac{k}{\mu}\bar{T}}{\bar{p}}\frac{\partial\rho}{\partial x_j}+\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}-\frac{1}{\bar{p}}\frac{\partial t_{\langle ij\rangle}}{\partial x_j}=0$$

$$\frac{\partial\frac{k}{\mu}\bar{T}}{\partial t}+\frac{2}{3}\frac{k}{\mu}\bar{T}\frac{\partial v_k}{\partial x_k}+\frac{2}{3}\frac{1}{\bar{p}}\frac{\partial q_k}{\partial x_k}=0$$

$$\frac{\partial t_{\langle ij\rangle}}{\partial t}-\frac{4}{5}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}-\frac{\partial p_{\langle ijk\rangle}}{\partial x_k}-2\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=-\frac{3}{2}\frac{1}{\tau}t_{\langle ij\rangle}$$

$$\frac{\partial q_i}{\partial t}-\frac{k}{\mu}\bar{T}\frac{\partial t_{\langle ik\rangle}}{\partial x_k}+\frac{5}{2}\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}=-\frac{1}{\tau}q_i$$

$$\frac{\partial p_{\langle ijk\rangle}}{\partial t}-3\frac{k}{\mu}\bar{T}\left(\frac{\partial t_{\langle ij\rangle}}{\partial x_{k\rangle}}-\frac{2}{5}\frac{\partial t_{\langle kl\rangle}}{\partial x_r}\delta_{jk\rangle}\right)=-\frac{9}{4}\frac{1}{\tau}p_{\langle ijk\rangle}$$

Lower left (Cattaneo):

$$\frac{\partial\rho}{\partial t}+\bar{p}\frac{\partial v_j}{\partial x_j}=0$$

$$\frac{\partial v_i}{\partial t}+\frac{\frac{k}{\mu}\bar{T}}{\bar{p}}\frac{\partial\rho}{\partial x_j}+\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}-\frac{1}{\bar{p}}\frac{\partial t_{\langle ij\rangle}}{\partial x_j}=0$$

$$\frac{\partial\frac{k}{\mu}\bar{T}}{\partial t}+\frac{2}{3}\frac{k}{\mu}\bar{T}\frac{\partial v_k}{\partial x_k}+\frac{2}{3}\frac{1}{\bar{p}}\frac{\partial q_k}{\partial x_k}=0$$

$$\frac{\partial t_{\langle ij\rangle}}{\partial t}-\frac{4}{5}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}-\frac{\partial p_{\langle ijk\rangle}}{\partial x_k}-2\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=-\frac{3}{2}\frac{1}{\tau}t_{\langle ij\rangle}$$

$$\frac{\partial q_i}{\partial t}-\frac{k}{\mu}\bar{T}\frac{\partial t_{\langle ik\rangle}}{\partial x_k}+\frac{5}{2}\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}=-\frac{1}{\tau}q_i$$

$$\frac{\partial p_{\langle ijk\rangle}}{\partial t}-3\frac{k}{\mu}\bar{T}\left(\frac{\partial t_{\langle ij\rangle}}{\partial x_{k\rangle}}-\frac{2}{5}\frac{\partial t_{\langle kl\rangle}}{\partial x_r}\delta_{jk\rangle}\right)=-\frac{9}{4}\frac{1}{\tau}p_{\langle ijk\rangle}$$

Lower right (13-moment theory):

$$\frac{\partial\rho}{\partial t}+\bar{p}\frac{\partial v_j}{\partial x_j}=0$$

$$\frac{\partial v_i}{\partial t}+\frac{\frac{k}{\mu}\bar{T}}{\bar{p}}\frac{\partial\rho}{\partial x_j}+\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}-\frac{1}{\bar{p}}\frac{\partial t_{\langle ij\rangle}}{\partial x_j}=0$$

$$\frac{\partial\frac{k}{\mu}\bar{T}}{\partial t}+\frac{2}{3}\frac{k}{\mu}\bar{T}\frac{\partial v_k}{\partial x_k}+\frac{2}{3}\frac{1}{\bar{p}}\frac{\partial q_k}{\partial x_k}=0$$

$$\frac{\partial t_{\langle ij\rangle}}{\partial t}-\frac{4}{5}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}-\frac{\partial p_{\langle ijk\rangle}}{\partial x_k}-2\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}=-\frac{3}{2}\frac{1}{\tau}t_{\langle ij\rangle}$$

$$\frac{\partial q_i}{\partial t}-\frac{k}{\mu}\bar{T}\frac{\partial t_{\langle ik\rangle}}{\partial x_k}+\frac{5}{2}\bar{p}\frac{k}{\mu}\bar{T}\frac{\partial\frac{k}{\mu}\bar{T}}{\partial x_i}=-\frac{1}{\tau}q_i$$

$$\frac{\partial p_{\langle ijk\rangle}}{\partial t}-3\frac{k}{\mu}\bar{T}\left(\frac{\partial t_{\langle ij\rangle}}{\partial x_{k\rangle}}-\frac{2}{5}\frac{\partial t_{\langle kl\rangle}}{\partial x_r}\delta_{jk\rangle}\right)=-\frac{9}{4}\frac{1}{\tau}p_{\langle ijk\rangle}$$

Fig. 14. Field equations for the 20-moment theory with mutilated cases in boxes: upper left: Euler fluid. Upper right: Navier-Stokes-Fourier fluid. Lower left: Cattaneo. Lower right: 13-moment theory.

In order to interpret the equations and relate them to the thermodynamic equations of balance and to the phenomenological equations we abandon the synthetic notation (7.13) and introduce the suggestive notation (7.7). Also we write the equations in the rest frame and linearize, meaning that we drop all products of linear terms. This has been done in Figure 14 which shows the field equations of the 20-moment theory four times in order to exhibit special cases: upper left through lower right. The frames indicate the forms of the field equations as specified in the legend of the figure: Euler, Navier-Stokes, Cattaneo[59], and 13 moments. We shall presently consider this. Note first, however, that the system is entirely specific: $\bar{p}$, $\bar{v}_i=0$, and $\bar{T}$ are the constant and time-independent values of density, velocity and temperature on which ρ, v_i, and T are superposed, and τ is the only parameter in the system. This parameter will shortly be related to the shear viscosity of the gas so that it may be considered as known.

The Euler fluid has no dissipative terms. Heat flux and deviatoric stress are ignored, and we know that this model is good enough for the calculation of the speed

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[59] Cf. Section 8.

of low-frequency sound and for the gross aspects of flow around obstacles. We also know its limitations: no dispersion, nor absorption of sound, and no boundary layers at obstacles.

The Navier-Stokes theory – upper right in Figure 14 – is more interesting for us. In the fourth and fifth equation we recognise the laws of Navier-Stokes and Fourier in the forms

$$t_{\langle ij \rangle} = \underbrace{\frac{4}{3}\tau\bar{p}}_{\text{shear viscosity}} \frac{\partial v_{\langle i}}{\partial x_{j\rangle}} \quad \text{and} \quad q_i = -\frac{5}{2}\tau\bar{p}\frac{\partial \frac{k}{\mu}T}{\partial x_i}. \qquad (7.25)$$

Thus the relaxation time τ determines the shear viscosity of the gas as indicated[60].

Note that the Navier-Stokes-Fourier theory requires the neglect of the gradients and rates of $t_{\langle ij \rangle}$ and q_i from the 4th and 5th equation. Thus it may be a proper and valid approximation, if gradients and rates are small. For processes with steep gradients and rapid rates, however, we must not ignore the derivatives of $t_{\langle ij \rangle}$ and q_i and so the laws of Navier-Stokes and Fourier become invalid. In that case the 13-moment theory provides the natural equations to fall back on. Since rates and gradients are measured in terms of mean times of free flight and mean free paths in gases, we come to the conclusion that 13 moments – and possibly more – are needed in rarefied gases, where collisions are rare and far-between.

We repeat that the systems of Figure 14 are fully explicit. This is also true for the 20-moment set which contains $\rho_{\langle ijk \rangle}$ in addition to the 13 variables ρ, v_i, $t_{\langle ij \rangle}$, q_i. $\rho_{\langle ijk \rangle}$ does not have a distinctive name, other than 3rd moment but it must obey an explicit set of equations. An essential difficulty is foreshadowed here because, in order to solve the – admittedly – specific system, we need boundary and initial values of the fields. And how would we adjust and control those values for the components of $\rho_{\langle ijk \rangle}$? We shall come back to that point later, see Section 9.8.

7.8 The 13-moment system

That problem with boundary values is minimised when we stick to the 13 moments ρ, v_i, T, $t_{\langle ij \rangle}$, and q_i, because all of those do have a suggestive meaning and – to some extent – we know how to adjust initial and boundary values for them. Therefore we summarise the above results for 13 moments and write – in an inertial frame –

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_n}{\partial x_n} = 0 \qquad \text{mass conservation}$$

$$\frac{\partial \rho v_i}{\partial t} + \frac{\partial F_{in}}{\partial x_n} = 0 \qquad \text{momentum conservation}$$

$$\frac{\partial F_{ii}}{\partial t} + \frac{\partial F_{njj}}{\partial x_n} = 0 \qquad \text{energy conservation}$$

$$\frac{\partial F_{\langle ij \rangle}}{\partial t} + \frac{\partial F_{\langle ij \rangle n}}{\partial x_n} = \Pi_{\langle ij \rangle}$$

$$\frac{\partial F_{ijj}}{\partial t} + \frac{\partial F_{ijjn}}{\partial x_n} = \Pi_{ijj}. \qquad (7.26)$$

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[60] The linear dependence of the shear viscosity on temperature through $p = \rho\frac{k}{\mu}T$ is an artifact caused by the assumption of Maxwellian atoms.

The decomposition (7.9) is understood and so is the closure by – according to (7.14), and (7.24) –

$$\Pi_{\langle ij\rangle} = \frac{1}{\tau}t_{\langle ij\rangle}, \qquad \Pi_{ijj} = -\frac{1}{\tau}\left(\frac{4}{3}q_i - 2v_j t_{\langle ij\rangle}\right),$$

$$\rho_{\langle ijk\rangle} = 0, \qquad \rho_{ijjk} = 5\rho\left(\frac{k}{\mu}T\right)^2 \delta_{ik} - 7\frac{k}{\mu}T t_{\langle ik\rangle}. \tag{7.27}$$

Therefore the system (7.26), (7.27) represents an explicit set of field equations.

7.9 Modification of Fourier's law in the 13-moment theory [Müller 2004]

Fourier's law has had a long life. Conceived in or about 1800, – as mentioned in Section 1 –, it formed an integral part of both Eckart's theory and of rational thermodynamics. Engineers are perfectly happy with it and there can be no doubt, that the law is correct for a wide range of circumstances. However it must be modified in rarefied gases, at least, if the kinetic theory of gases is to be believed. Let us consider this.

On the basis of the arguments of Section 7.7 we assume that the rarefied gas may satisfy the equations of the 13-moment theory. For illustration of its results we consider a situation as shown in Figures 2 and 10: stationary heat conduction in a gas at rest between two co-axial cylinders. The heating $\dot{q}$ is applied to the inner cylinder while the outer one is kept at the temperature T_{ext}. The mass balance is identically satisfied in this case and the other 12 equations of balance read, by (7.26) and (7.27)[61]

$$\rho^{ik}; k = 0$$

$$\rho^{ijk}; k = -\frac{3}{2}\frac{1}{\tau}\rho^{\langle ij\rangle} \qquad \text{where} \qquad \rho^{ijk} = \frac{2}{5}\left(q^i g^{jk} + q^j g^{ik} + q^k g^{ij}\right)$$

$$\rho^l l^{ik}; k = -\frac{2}{\tau}q^i \qquad \text{where} \qquad \rho^l l^{ik} = 5\rho\left(\frac{k}{\mu}T\right)^2 g^{ik} - 7\frac{k}{\mu}T t^{\langle ik\rangle}. \tag{7.28}$$

We look for solutions in which all fields depend on the radial variable only and in which the heat flux has only a radial component. Under the assumption of a constant τ the solution is analytic[62], the pressure $p = \rho\frac{k}{\mu}T$ is homogeneous, all shear stresses vanish, but the normal components of the deviatoric stress *do not*. We obtain

$$\rho^{\langle 11\rangle} = \frac{8}{15}\tau\frac{1}{r}q^1, \qquad \rho^{\langle 22\rangle} = -\frac{8}{15}\tau\frac{1}{r^3}q^1, \qquad \rho^{\langle 33\rangle} = 0, \qquad \text{and}$$

$$q^1 = -\frac{5}{2}\frac{k}{\mu}p\tau\left(1 + \frac{7}{5}\frac{\rho^{\langle 11\rangle}}{p}\right)\frac{dT}{dr}. \tag{7.29}$$

This solution is essentially different from a Navier-Stokes-Fourier fluid, because there are no deviatoric stresses in a gas at rest according to the Navier-Stokes equations,

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[61] It is appropriate in this case of cylindrical symmetry to chose cylindrical coordinates $(x^1, x^2, x^3) = (r, \theta, z)$ and co- or contravariant components of the tensors. A semicolon denotes covariant derivatives and g^{ik} is the metric tensor. The Christoffel symbols are given by $\Gamma_{12}^1 = -r$, $\Gamma_{12}^2 = \Gamma_{21}^2 = 1/r$, $\Gamma_{jk}^i = 0$ else.

[62] τ depends on the density of course and, if we take that fact into account, we have to use numerical means to solve the equations. Quantitatively that numerical solution is similar to the analytic solution calculated here and represented in Figure 15.
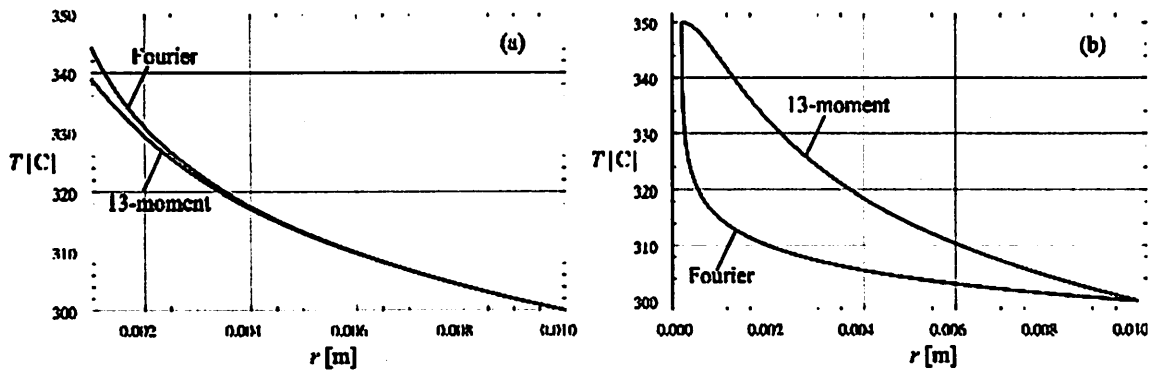
Fig. 15. Comparison of temperature fields according to Fourier's solution and the 13-moment solution. Parameters: $p = 10^2$ N/m^2, $\tau = 10^{-5}$ s. (a) Boundary values: $\dot{q} = 10^4$ W/m^2 at $r_{int} = 10^{-3}$ m, $T = 300$ K at $r_{ext} = 10^{-2}$ m. (b) Boundary values: $T = 350$ K at $r_{int} = 2.5 \times 10^{-6}$ m, $T = 300$ K at $r_{ext} = 10^{-2}$ m.

and in the Fourier theory the heat flux is unaffected by the stress. The Fourier law is recovered from (7.29), when we neglect terms with τ^2.

Insertion of (7.29) into the energy balance $\frac{dq^1}{dr} + \frac{1}{r}q^1 = 0$ provides an explicit differential equation for T with the solution

$$T = c_2 - \frac{c_1}{5\frac{k}{\mu}p\tau} \ln\left(r^2 + \frac{56}{75}\frac{\tau}{p}c_1\right). \tag{7.30}$$

Obviously the second term in the argument of the logarithm makes this equation different from Fourier's solution. c_1 and c_2 are constants of integration that depend on boundary conditions. Figure 15a shows solutions for the case that the gas is kept at a fixed temperature at the outer cylinder, while at the inner cylinder it is heated. Inspection shows, as expected, that the 13-moment theory differs from Fourier's where the temperature field is steep. Actually the difference is not only quantitative, because for a given heating, i.e. given c_1, Fourier's solution has a logarithmic singularity when the inner radius tends to zero. The 13-moment solution, on the other hand, has no such singularity.

Figure 15b again compares the solution (7.30) and the Fourier solution, but it refers to the case that the temperatures are prescribed on both boundaries. Moreover the inner cylinder is very thin in Figure 15b namely 2.5×10^{-6} m, – appropriate for a hot wire anemometer. The discrepancy is now very drastic indeed: the temperature graph is not even convex anymore for the 13-moment solution.

A caution is appropriate concerning the validity of the 13-moment theory in the case of Figure 15b, because we do not know a priori how far that theory can be relied upon. The gradient of the Fourier solution is very steep close to the hot wire and it may well be that we need *more* than 13-moments to deal with the case. That can be checked, of course, namely by solving the equations for 20, or 35 moments. If they differ, – and if they differ from the 13-moment case –, we must conclude that we need 56 moments, or even 84 of them, or more[63]. Eventually we expect convergence and when that happens we may read off the proper number of moments for a given physical situation. Such a strategy is carried out in Section 9 for light scattering, but not here in the present case.

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[63] The numbers are those for all components of moments of rank 3, 4, and 5, and 6. In general, i.e. for rank N, we have $1/6(N+1)(N+2)(N+3)$ moments.

There is a potentially interesting corollary concerning the 13-moment non-convective entropy flux between the two cylinders. Its radial component comes out as

$$\varphi^r = \frac{1}{T}\left(1 - \frac{2}{5}\frac{\rho^{\langle rr\rangle}}{p}\right)q^r$$

so that at a wall, which is free of dissipation, i.e. entropy production, the quantity

$$\theta = \frac{T}{1 - \frac{2}{5}\frac{\rho^{\langle rr\rangle}}{p}}$$

is continuous. We may be tempted to call this quantity θ the *thermodynamic temperature*[64]. Clearly it is different from the previously defined *kinetic temperature* T, see Section 7.2 above. For a discussion of this aspect and for the size of the difference between θ and T see [Müller 2003]. For data like those in Figure 15 the difference between the kinetic and the thermodynamic temperature amounts to a few degree °C.

Another interesting – *qualitatively* interesting – consequence of the 13-moment theory concerning heat conduction in a gas between co-axial cylinders is this: *the gas cannot rotate rigidly* on account of the Coriolis force on the molecular motion. Indeed, in a non-inertial frame there is no solution with $v_i = 0$, if heat is being conducted. To be sure, the radial velocity may be zero, but the azimuthal one cannot be zero. See [Barbera 2006].

7.10 Finite speeds of propagation

Now, since we have a modified Fourier law, it is possible to ask whether or not the new theory still implies the *paradox of heat conduction*, i.e. an infinite speed of propagation (see Sect. 1.2). It does not! The easiest way to see this is the calculation of the possible phase speeds of plane harmonic waves with small amplitudes. Such waves are best represented by an exponential ansatz in which the fields ρ, v_1, T, $t_{\langle 11\rangle}$, q_1 are all proportional to $\exp[i(\omega t - kx)]$ with complex amplitudes[65]. The wave propagates in the x-direction, ω is its frequency, and k is the complex wave number, whose real part is the actual wave number, while the imaginary part represents the attenuation of the wave. The phase speed is given by

$$v_{Ph} = \frac{\omega}{\mathrm{Re}(k)}.$$

It depends on ω and in general there is more than one mode of propagation. It can be shown, e.g. see [Müller 1998], that the fastest speed $v_{Ph}^{\max}$ of each mode is equal to $v_{Ph}(\omega \to \infty)$.

When the exponential ansatz is introduced into the 13-moment system of Figure 14, one obtains a linear harmonic system of equations. For the existence of a non-trivial solution the determinant must vanish and that requirement leads to the *dispersion relation*

$$\left(i\frac{3}{2} - \frac{9}{5}\omega\tau\right)\left(\frac{k}{\omega/v_0}\right)^4 - \left(\frac{5}{2}\frac{1}{\omega\tau} + 8i - \frac{26}{5}\omega\tau\right)\left(\frac{k}{\omega/v_0}\right)^2 + \left(\frac{5}{2}\frac{1}{\omega\tau} + i\frac{25}{6} - \frac{5}{3}\omega\tau\right) = 0 \tag{7.31}$$

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[64] Recall that in thermodynamics the temperature is defined as *the* quantity that is continuous at a thermometric (sic) wall. In non-equilibrium the so-defined temperature may well be different from T.

[65] The actual fields are given by either the real or the imaginary parts of the ansatz.

which provides k as a function of[66] ω. We obtain four solutions – two each in the plus direction and the minus direction – and their phase speeds read in the high-frequency limit

$$v_{Ph}^{(1)^{max}} = 1.65 v_0 \quad \text{and} \quad v_{Ph}^{(2)^{max}} = 0.63 v_0. \tag{7.32}$$

Thus no paradox occurs. The highest speed of propagation is $v_{Ph}^{(1)^{max}}$. We call it the *pulse speed*. And that pulse speed, far from being infinite, is not much larger than the ordinary sound speed v_o.

Once again, like in mixtures and – in fact – like in a Navier-Stokes-Fourier single gas, there are two modes of propagation, or two sounds. However, only *one*, the one starting with v_o at $\omega \to 0$ and ending with $v_{Ph}^{(1)^{max}}$ at $\omega \to \infty$, is ever heard, because the other one is strongly damped. More about pulse speeds in Sections 8 and 9.

7.11 Entropy and entropy flux for 13 moments

Given the 13-moment distribution f^{13} we may calculate explicit expressions for the specific entropy and the non-convective entropy flux from $(7.17)_{1,2}$. If the logarithm is expanded – assuming the non-equilibrium part of f^{13} as small – we obtain

$$s = s_E - \frac{k}{\mu} \left(\frac{1}{4} \frac{t_{\langle ij \rangle} t_{\langle ij \rangle}}{p^2} + \frac{1}{5} \frac{q^2}{p^2 \frac{k}{\mu} T} \right), \qquad \varphi_i = \frac{q_i}{T} + \frac{2}{5} \frac{t_{\langle ij \rangle} q_j}{pT}. \tag{7.33}$$

Thus the kinetic theory contradicts Eckart's principle of local equilibrium, because the entropy depends on non-equilibrium variables, viz. $t_{\langle ij \rangle}$ and q_i. Similarly the entropy flux is not equal to the Clausius-Duhem expression q_i/T, as it is in Eckart's theory. This latter result has provided the motivation for considering the entropy flux as a constitutive quantity in its own right, a priori unrelated to the heat flux, see Sections 5 and 8.

It is true that the non-conventional terms in (7.33) are non-linear; that fact does make them small, if we are close to equilibrium, but not negligible, because the entropy balance contains non-linear terms routinely. Without such terms the inequality becomes trivial: it is reduced to an equality and no irreversibility occurs.

8 Extended thermodynamics

8.1 Abstract

Extended thermodynamics of a single gas was developed in the past 60 years in three stages of increasing mathematical sophistication and significance.

In 1948 Cattaneo's early effort to resolve the paradox of heat conduction has called attention to an elementary form of the kinetic theory of gases from which an improved form of the Fourier law could be derived, a rate law for the heat flux [Cattaneo 1948]. Cattaneo's success created an interest among thermodynamicists in the formal kinetic theory based on 13 moments. This is vastly more intricate than Cattaneo's original equation, but it contains that equation when properly mutilated. Thus in a heuristic manner irreversible thermodynamics was joined to the kinetic theory.

Afterwards it was recognised by Liu and Müller that Grad's 13-moment theory – based on full moments rather than internal ones – provides a simple scheme of balance equations for whose constitutive equations the entropy inequality could be exploited

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[66] $v_0 = \sqrt{\frac{5}{3} \frac{k}{\mu} T}$ is the speed of the low-frequency sound, the one we actually hear.

systematically with the use of Lagrange multipliers [Liu 1983]. The results of this type of extended thermodynamics were much like those of the kinetic theory itself.

That systematic theory prepared extended thermodynamics for a merger with the theory of symmetric hyperbolic systems which mathematicians had become interested in when the Burgers equation – the simple prototype of hyperbolic equations, see Sect. 2.8 – was fully exploited. The close relation of the two theories was recognised by Ruggeri and Strumia. Thus they were able to make extended thermodynamics a fully legitimate part of mathematical physics [Ruggeri 1981]. The formal structure of that theory exhibits a decisive role for the Lagrange multipliers [Boillat 1974].

8.2 Heuristic beginnings. Resolution of paradoxes

The original, in retrospect rather naïve motive for the development of extended thermodynamics was the *paradox of heat conduction*, so called by Cattaneo in 1948 (see Preview and Sect. 1.1). The paradox results from the parabolic character of the heat equation (1.2) which implies an infinite propagation speed of temperature changes. This was discussed in Section 1.

Upon reflection it was clear to Cattaneo that Fourier's law (1.1) was to blame, and that the law had to be modified. We best understand his argument by referring to Section 1.3, and Figure 2 within that section, which provides an atomistic interpretation of the Fourier law. That interpretation is valid provided that the situation is stationary. If it is *not* stationary, the energy transfer of the two atoms crossing the plane H-H is no longer proportional to the temperature gradient at the time of passage through H-H; rather it is proportional to the gradient at a slightly earlier time, namely when the atoms started out from the top and bottom of the small element shown in Figure 2. Using a Taylor expansion for the history of the temperature gradient we might therefore expect that the heat flux should be given by

$$q_i = -\kappa\left(\frac{\partial T}{\partial x_i} - \tau\frac{\partial}{\partial t}\left(\frac{\partial T}{\partial x_i}\right)\right) \quad \text{or equivalently} \quad \frac{1}{1-\tau\frac{\partial}{\partial t}}q_i = -\kappa\frac{\partial T}{\partial x_i}, \quad (8.1)$$

where obviously τ must be positive, since $t - \tau$ is a time in the past. This seems like a plausible argument. And yet, when the relation (8.1) is used in the energy equation $\rho c\frac{\partial T}{\partial t} + \frac{\partial q_i}{\partial x_i} = 0$, we obtain

$$\frac{\partial T}{\partial t} + \frac{\kappa\tau}{\rho c}\frac{\partial}{\partial t}\left(\frac{\partial^2 T}{\partial x_i\partial x_i}\right) - \frac{\kappa}{\rho c}\frac{\partial^2 T}{\partial x_i\partial x_i} = 0,$$

an equation which – ironically – is *still* parabolic and predicts infinite speed.

Cattaneo does not comment on the calamity. He must have noticed it, however, because he proceeds with a bit of *creative mathematics* involving an approximation of the operator in $(8.1)_2$ like this

$$\frac{1}{1-\tau\frac{\partial}{\partial t}} \approx 1 + \tau\frac{\partial}{\partial t}. \quad (8.2)$$

Thus (8.1) turns into what is now known as the *Cattaneo equation*, a rate law for the energy flux

$$\tau\frac{\partial q_i}{\partial t} + q_i = -\kappa\frac{\partial T}{\partial x_i}. \quad (8.3)$$

When q_i is *now* eliminated between the energy equation and the Cattaneo equation, we obtain

$$\tau\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \frac{\kappa}{\rho c}\frac{\partial^2 T}{\partial x_i\partial x_i} \quad (8.4)$$

and this is the telegraph equation, a prototypical hyperbolic equation of second order in mathematical physics. It predicts the propagation of damped temperature waves and – for normal conditions in a gas – it implies a speed of propagation

$$V = \sqrt{\frac{\kappa}{\rho c_T}} \approx 10^2 - 10^3 \; \frac{m}{s}.$$

Thus for Cattaneo the paradox was resolved and this was as far as he went. Even now many people consider the Cattaneo equation as the ultimate achievement of extended thermodynamics, a goal reached, and a problem satisfactorily solved[67].

However, this was just the beginning of proper extended thermodynamics, because there are a number of subtle aspects to be considered. First of all, the paradox of heat conduction is not alone: there are analogous paradoxes of diffusion and of the propagation of shear waves, and these are due to the laws of Fick[68] and Navier-Stokes, respectively. Indeed, the law of Navier-Stokes, viz.

$$t_{\langle ij \rangle} = 2\eta \frac{\partial v_{<i}}{\partial x_{j>}}$$

between stress and shear rate is quite analogous in its structure and atomistic interpretation to Fourier's law. For a non-stationary shear rate we might therefore be tempted to repeat Cattaneo's reasoning and write the equations

$$t_{\langle ij \rangle} = 2\eta \left(\frac{\partial v_{<i}}{\partial x_{j>}} - \tau \frac{\partial}{\partial t} \left(\frac{\partial v_{<i}}{\partial x_{j>}} \right) \right) \quad \text{and then} \quad \tau \frac{\partial t_{\langle ij \rangle}}{\partial t} + t_{\langle ij \rangle} = 2\eta \frac{\partial v_{<i}}{\partial x_{j>}}; \quad (8.5)$$

the latter by the *creative trick* indicated in (8.2).

Equation (8.5)$_1$ may create a feeling of *déjà vu* in the attentive reader. Indeed, we have seen that equation before[69], – see Sect. 5.5, Eq. (5.3) – and we have dismissed it, along with rational thermodynamics of non-Newtonian fluids, on the grounds of stability. In the same manner Cattaneo's first equation (8.1) predicts instability: for $q_i = 0$ the temperature gradient *rises* exponentially! Cattaneo's second equation (8.3) on the other hand does not show this type of instability: for $\frac{\partial T}{\partial x_i} = 0$ the heat flux *decays* exponentially as is to be expected. Therefore we conclude that *rate laws* of the

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[67] The careful reader will have noticed that the present argument differs slightly from the previous one in the Preview, cf. (P.1) through (P.4), although the formulae are the same ones. In the present case the previously essential Taylor expansion arises naturally and there is not really any mention of the history of the temperature gradient. The two approaches represent two aspects of the same phenomenon, although the present one – Cattaneo's original one – is more intuitively plausible, perhaps, because it is based on a suggestive molecular argument. On the other hand, the Cattaneo equation may be integrated to give

$$q_i(t) = -\frac{\kappa}{\tau} \int\limits_{-\infty}^{t} \exp\left(-\frac{t-t'}{\tau}\right) \frac{\partial T(x_j, t')}{\partial x_i} dt',$$

and that formula emphasizes the history-aspect discussed before [Grioli 1979].

[68] Extended thermodynamics of mixtures – see Section 6 – has resolved the paradox of diffusion by adding the acceleration of the diffusive motion to Fick's law. That theory seems satisfactory as far as it goes. It concentrates on diffusion; heat conduction and viscous stresses are ignored, so that nothing is said in it about the paradoxa of heat conduction and shear rates.

[69] Actually we have also seen Cattaneo's first equation (8.1) before, namely when we considered the Chapman-Enskog approximation in Section 7.6 and its inherent instability.

types (8.3) and (8.5)$_2$ for heat flux and stress are good, while *differential laws* of the types (8.1) and (8.5)$_1$ are bad. The differential laws lead to instability and infinite speeds.

It is not immediately clear *why* one type of law should be preferred over the other, at least not within a *macroscopic* theory. The reason lies in the more basic *microscopic* description of continuous bodies. Indeed, all microscopic theories of continua are based on transport equations, like the Boltzmann equation for a gas, and they invariably exhibit a time derivative and a gradient of a distribution function, and a production. The time derivative leads to rate laws and, under many circumstances, it gives a small contribution to the macroscopic equations and is therefore neglected; however, *it is there* and it determines stability and propagation.

We observe that the modified laws of Fourier and Navier-Stokes – equations (8.3) and (8.5)$_2$ – are uncoupled. This, however, is an artefact of an oversimplified derivation. In reality there are coupling terms, but they are too complex to be derivable by elementary kinetic reasoning like those of the Cattaneo argument. In order to derive the proper equations we need the full complexity of the Boltzmann equation, or of the moment equations (7.13) based on it. If these equations are closed by use of Grad's 13-moment distribution, some rearrangement leads to equations for the heat flux and the stress of the form

$$q_i = -\frac{15}{4}\frac{k}{\mu}p\tau\left\{\frac{\partial T}{\partial x_i} + \frac{2}{5\frac{k}{\mu}}\frac{1}{p}\left[\dot{q}_i + q_n\frac{\partial v_i}{\partial x_n} - 2q_nW_{in}\right] + \frac{2}{5}\frac{T}{p}\frac{\partial t_{\langle in\rangle}}{\partial x_n}\right\} -$$

$$\boxed{-\frac{3}{2}\tau\left(\frac{7}{5}q_i\frac{\partial v_n}{\partial x_n} + \frac{4}{5}q_n\frac{\partial v_{\langle i}}{\partial x_{n\rangle}} - \frac{7}{2}\frac{k}{\mu}t_{\langle ik\rangle}\frac{\partial t_{\langle kn\rangle}}{\partial x_n} + \frac{1}{\rho}t_{\langle ik\rangle}\frac{\partial p}{\partial x_k}\right)}$$

$$t_{\langle ij\rangle} = 2p\rho\left\{\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \frac{1}{2p}\left[\dot{t}_{\langle ij\rangle} + 2t_{\langle n\langle i\rangle}\frac{\partial v_{j\rangle}}{\partial x_{n\rangle}} - 4t_{\langle n\langle i\rangle}W_{j\rangle n}\right] + \frac{2}{5}\frac{1}{p}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}}\right\} -$$

$$\boxed{-\frac{1}{\tau}t_{\langle ij\rangle}\frac{\partial v_n}{\partial x_n}} \qquad\qquad (8.6)$$

In the underlined terms we recognise the Cattaneo equation and the previously discussed extended Navier-Stokes law. However the equations are a lot more complex, so much so that not all terms can be given suggestive interpretations. The framed terms are non-linear and, even if we ignore those, the heat flux and stress are now coupled. Moreover, the simple partial time derivatives $\frac{\partial q_i}{\partial t}$ and $\frac{\partial t_{\langle ij\rangle}}{\partial t}$ in (8.3) and (8.5)$_2$ are now replaced by the Euclidean tensors

$$\left[\dot{q}_i + q_n\frac{\partial v_i}{\partial x_n} - 2q_nW_{in}\right] \quad\text{and}\quad \left[\dot{t}_{\langle ij\rangle} + 2t_{\langle n\langle i\rangle}\frac{\partial v_{\langle j\rangle}}{\partial x_{n\rangle}} - 4t_{\langle n\langle i\rangle}W_{j\rangle n}\right], \qquad (8.7)$$

which involve the angular velocity W_{ij} of the frame. Those are vectors and tensors, respectively, which $\frac{\partial q_i}{\partial t}$ and $\frac{\partial t_{\langle ij\rangle}}{\partial t}$, or even $\dot{q}_i$ and $\dot{t}_{\langle ij\rangle}$ – the material time derivatives – alone are not.

It may be worthwhile to mention here that the expressions

$$\left[\dot{q}_i - q_n\frac{\partial v_i}{\partial x_n}\right] \quad\text{and}\quad , \left[\dot{t}_{\langle ij\rangle} - 2t_{\langle n\langle i\rangle}\frac{\partial v_{\langle j\rangle}}{\partial x_{n\rangle}}\right] \qquad (8.8)$$

also represent an Euclidean vector and tensor, respectively. They provide the rates of change of q_i and $t_{\langle ij\rangle}$ in the co-rotational frame of the gas, and they might be the first choice of a scientist to replace $\frac{\partial q_i}{\partial t}$ and $\frac{\partial t_{\langle ij\rangle}}{\partial t}$ in the Cattaneo equation, or in (8.5)$_2$, if

he wishes to convert those relations into a proper tensorial form. However, that would run against the dictate of the kinetic theory of gases.

As was explained before, equations (8.6) were first found in the kinetic theory of gases as parts of Grad's 13-moment theory. Müller succeeded to derive them from TIP – Eckart's theory – albeit without the non-linear terms and with arbitrary coefficients instead of $\frac{7}{5}\frac{k}{\mu}$, $\frac{2}{5}\frac{T}{p}$, etc. [Müller 1966]. He achieved that by giving up the principle of local equilibrium and without the a priori assumption that the entropy flux is given by heat flux over temperature. Thus Müller demonstrated that the doctrine of forces and fluxes could be used to obtain specific results that had formerly seemed to require the knowledge of the distribution function of the kinetic theory. Müller dubbed his extension of Eckart's arguments *extended thermodynamics*[70].

Yet, the complexity of equations (8.6) is such that no system of field equations, of which they are a part, can be characterised as parabolic or hyperbolic, at least not without considerable effort. Therefore extended thermodynamics could only *take off* as a reasonable branch of mathematical physics after a more concise formulation was found. Such a formulation appeared with the work of Liu and Müller [Liu 1983]. They cast equations (8.6) into an elegant balance form, see Section 8.3 below, and they employed Lagrange multipliers and Galilean invariance, so that the doctrine of forces and fluxes was no longer needed. We proceed to look at this in the next section.

The heuristic version of extended thermodynamics was adopted by a group of mostly Spanish physicists and it gained some popularity by their book, entitled Extended Irreversible Thermodynamics [Jou 1993]. The authors follow the line of giving up the principle of local equilibrium and the restrictive relation between the fluxes of entropy and heat. A possibly pregnant trait of that theory is the application to non-Newtonian fluids where the time derivatives in (8.3) and (8.5)$_2$ are replaced by the co-rotational derivatives (8.8). The kinetic theory of polymer solutions shows that this is the proper choice for rheological fluids, just like the choice (8.7) is proper for gases according to the kinetic theory of gases. Extended thermodynamics may well turn out in the future to be an innovative theory for non-Newtonian fluids. A pre-condition for that to happen seems to be a close study and extrapolation of existing kinetic theories of macro-molecular solutions, see [Bird 1971; Curtis 1976; Müller 1979]. The theory may then achieve a satisfactory mathematical structure which, so far, it does not have. The task is a lot more difficult than for gases and Newtonian fluids, where it has already reached a conclusion of sorts, see Section 8.4 below.

8.3 Extended thermodynamics of 13 moments

Starting point is the set of the 13 balance equations (7.26)

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_n}{\partial x_n} = 0 \qquad \text{mass conservation}$$

$$\frac{\partial \rho v_i}{\partial t} + \frac{\partial F_{in}}{\partial x_n} = 0 \qquad \text{momentum conservation}$$

$$\frac{\partial F_{ii}}{\partial t} + \frac{\partial F_{njj}}{\partial x_n} = 0 \qquad \text{energy conservation}$$

$$\frac{\partial F_{\langle ij \rangle}}{\partial t} + \frac{\partial F_{\langle ij \rangle n}}{\partial x_n} = \Pi_{\langle ij \rangle}$$

$$\frac{\partial F_{ijj}}{\partial t} + \frac{\partial F_{ijjn}}{\partial x_n} = \Pi_{ijj}, \qquad\qquad\qquad (8.9)$$

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[70] Or, actually, in German: *Erweiterte Thermodynamik*. The Gibbs equation was generalized – or *extended* – because the entropy was supposed to depend on the heat flux and the deviatoric stress.

which are supplemented by constitutive equations of the form

$$F_{\langle ij \rangle n} = \hat{F}_{\langle ij \rangle n} \left(\rho, v_i, T, F_{\langle pq \rangle}, F_{llp} \right)$$

$$F_{ijjn} = \hat{F}_{ijjn} \left(\rho, v_i, T, F_{\langle pq \rangle}, F_{llp} \right)$$

$$\Pi_{\langle ij \rangle} = \hat{\Pi}_{\langle ij \rangle} \left(\rho, v_i, T, F_{\langle pq \rangle}, F_{llp} \right)$$

$$\Pi_{ijj} = \hat{\Pi}_{ijj} \left(\rho, v_i, T, F_{\langle pq \rangle}, F_{llp} \right) \tag{8.10}$$

in order to obtain field equations for the 13 fields ρ, v_i, T, $F_{\langle ij \rangle}$, F_{lli}.

The constitutive functions $\hat{F}$ and $\hat{\Pi}$ in (8.10) are assumed to be invariant under Galilean transformations and the solutions of the system of equations (8.9), (8.10) are called *thermodynamic processes*.

The entropy inequality has the generic form

$$\frac{\partial h}{\partial t} + \frac{\partial h_i}{\partial x_i} \geq 0, \tag{8.11}$$

where h is the entropy density and h_i the entropy flux – convective *and* non-convective. Both are given by constitutive relations

$$h = \hat{h} \left(\rho, v_i, T, F_{\langle pq \rangle}, F_{llp} \right)$$

$$h_i = \hat{h}_i \left(\rho, v_i, T, F_{\langle pq \rangle}, F_{llp} \right). \tag{8.12}$$

The inequality is assumed to hold for all thermodynamic processes. This latter qualification, i.e. the restriction to thermodynamic processes, may be eliminated by the use of Lagrange multipliers. Indeed, Liu has shown that the larger inequality

$$\frac{\partial h}{\partial t} + \frac{\partial h_i}{\partial x_i} - \Lambda \left(\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_i}{\partial x_i} \right) - \Lambda^i \left(\frac{\partial \rho v_i}{\partial t} + \frac{\partial F_{in}}{\partial x_n} \right) - \Lambda_{ii} \left(\frac{\partial F_{ll}}{\partial t} + \frac{\partial F_{nll}}{\partial x_n} \right)$$

$$- \Lambda_{\langle ij \rangle} \left(\frac{\partial F_{\langle ij \rangle}}{\partial t} + \frac{\partial F_{\langle ij \rangle n}}{\partial x_n} - \Pi_{\langle ij \rangle} \right) - \Lambda_{ill} \left(\frac{\partial F_{inn}}{\partial t} + \frac{\partial F_{illn}}{\partial x_n} - \Pi_{ill} \right) \geq 0 \tag{8.13}$$

must hold for *all fields* ρ, v_i, T, $F_{\langle ij \rangle}$, F_{ijj} [Liu 1972a; 1972b]. The auxiliary Lagrange multipliers Λ are functions of the variables listed in (8.10) or (8.12), and those functions are to be determined – or eliminated – in the process of the exploitation of the inequality (8.13).

The exploitation leads to specific forms of all constitutive functions. Within a linearised theory the results read

$$\rho_{\langle ijk \rangle} = 0, \qquad \rho_{ijjk} = 5\rho \left(\frac{k}{\mu} T \right)^2 \delta_{ik} - 7 \frac{k}{\mu} T t_{\langle ik \rangle},$$

$$\Pi_{\langle ij \rangle} = \frac{1}{\tau_t} t_{\langle ij \rangle} \qquad \text{and} \qquad \Pi_{ijj} = -\frac{2}{\tau_q} q_i + \frac{1}{\tau_t} t_{\langle ij \rangle} v_j, \tag{8.14}$$

just like in (7.24) and (7.14) in the kinetic theory.

Moreover, the specific entropy and the entropy flux come out as

$$h = \rho s_E - \frac{k}{\mu} \rho \left(\frac{1}{4} \frac{t_{\langle ij \rangle} t_{\langle ij \rangle}}{p^2} + \frac{1}{5} \frac{q^2}{p^2 \frac{k}{\mu} T} \right) \quad \text{and} \quad h_i = \rho h v_i + \frac{q_i}{T} + \frac{2}{5} \frac{t_{\langle ij \rangle} q_j}{pT} \tag{8.15}$$

just like in (7.33).

These results, viz. (8.14) and (8.15), derived by the exploitation of the inequality (8.13), required extensive calculations, mostly for the elimination of the auxiliary Lagrange multipliers. The theory was applied to classical as well as degenerate monatomic gases[71] [Liu 1983]. That paper was greeted with some surprise, because it recovered so many of the explicit results of the kinetic theory. Thus it showed to what extent some specific assumptions of that theory were not needed in thermodynamics, particularly the moment-character of the F's, and the specific form of the 13-moment distribution function.

What *was* needed was a lot less specific, viz.

- the balance structure of the field equations;
- local and instantaneous dependence of the constitutive quantities upon the variables; and
- the Galilean invariance of the system of field equations which guarantees the decomposition of the F's into the ρ's.

In order to avoid repetition we do not go any deeper into this approach. Indeed, in the next section we proceed to formulate the fully formal theory of extended thermodynamics, which was largely motivated by the observations just indicated here. In fact, extended thermodynamics was now prepared to be joined to the mathematical theory of hyperbolic systems that had grown out of the study of the Burgers equation. Both theories inspired and stimulated each other and the Lagrange multipliers – originally introduced as purely auxiliary quantities – turned out to constitute a privileged field for which the field equations are symmetric hyperbolic. Such a property provides a number of benefits of which finite speeds are only one.

Let us proceed to consider that formal theory which we regard as the summary – and generalisation – of all that has been said and done on extended thermodynamics before.

8.4 Formal structure of extended thermodynamics

8.4.1 Thermodynamic processes

Let $u_\alpha(x_i, t)$ ($\alpha = 0, 1, \ldots n - 1$) denote n fields that we wish to determine and let the necessary field equations have balance form

$$\frac{\partial u_\alpha}{\partial t} + \frac{\partial F_{d\alpha}}{\partial x_d} = \Pi_\alpha \qquad (\alpha = 0, 1, \ldots n - 1). \tag{8.16}$$

We call u_α *densities*. $F_{d\alpha}$ and Π_α are *fluxes* and *productions* respectively, and we consider them as constitutive quantities which depend on the material of the body under consideration. Extended thermodynamics assumes that the constitutive relations are local and instantaneous so that $F_{d\alpha}$ and Π_α at one point and time depend on the densities u_α at that point and time only

$$F_{d\alpha} = \hat{F}_{d\alpha}(u_\beta) \qquad \text{and} \qquad \Pi_\alpha = \hat{\Pi}_\alpha(u_\beta). \tag{8.17}$$

In particular, no gradients and rates of change occur among the independent variables.

If the constitutive functions $\hat{F}_{d\alpha}$ and $\hat{\Pi}_\alpha$ are known explicitly, we may eliminate $F_{d\alpha}$ and Π_α between (8.16) and (8.17) and arrive at an explicit set of field equations. Every solution of those is called a *thermodynamic process*.

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[71] To be sure, Liu and Müller do not get $\Pi_{\langle ij \rangle}$ and Π_{ii} with one single relaxation time τ as does the kinetic theory. Rather they have two relaxation times, one each for the stress and the heat flux.

Thus, in effect we have reduced extended thermodynamics to the two lines (8.16), (8.17). And that is all there is to it, if indeed, we do know the constitutive functions. In reality, however, those functions are unknown and we must attempt to determine them, or at least restrict them in their generality and, perhaps, reduce them to a few coefficients which may then be measured. This is the task of the *constitutive theory* and most thermodynamicists work on that task.

Note that the field equations form a system of n quasilinear partial differential equations of first order. This is the structure suggested by the moment equations of the kinetic theory of gases, cf. (7.12), (7.13). To be sure, the moment equations (7.12), (7.13) are simpler than the present equations (8.16), because in the kinetic theory – of monatomic gases – the flux in one equation doubles as the density in the following equation so that only *one* flux, namely $F_{i_1...i_N d}$ – the last one – needs to be given for the closure of the system.

The quasi-linear system of equations composed of (8.16), (8.17) has caught the attention of mathematicians. It is the natural extension of the Burgers equation, see equation (2.17). Friedrichs and Lax have shown that the multiplication of (8.16) by a positive definite Hessian matrix $\frac{\partial^2 \eta}{\partial u_\gamma \partial u_\alpha}$ leads to a symmetric hyperbolic system of equations. Such systems are attractive to mathematicians because of the well-posedness of initial value problems and, in particular, finite speeds, see below [Friedrichs 1971]. A drawback of the Friedrichs and Lax-approach is that multiplication by $\frac{\partial^2 \eta}{\partial u_\gamma \partial u_\alpha}$ destroys the balance character of the equations and therefore the possibility to deal with shock waves. Extended thermodynamics avoids that drawback, because it produces symmetric hyperbolic systems by a transformation of variables as we shall see; the discovery of that transformation is due to Boillat [Boillat 1974].

The synthetic notation in (8.16), (8.17) may be confusing to a thermodynamicist brought up in (p, V, T)-thermodynamics. So, let it be said that the first five among equations (8.16) are invariably the conservation laws of mass, momentum and energy and their productions are zero. They read

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_i}{\partial x_i} = 0$$

$$\frac{\partial \rho v_j}{\partial t} + \frac{\partial \left(\rho v_j v_i - t_{ij} \right)}{\partial x_i} = 0$$

$$\frac{\partial \rho \left(u + \frac{1}{2} v^2 \right)}{\partial t} + \frac{\partial \left(\rho \left(u + \frac{1}{2} v^2 \right) v_i - t_{ij} v_j + q_i \right)}{\partial x_i} = 0. \tag{8.18}$$

The productions $\Pi_\alpha (\alpha = 0, 1 \ldots 4)$ vanish, because mass, momentum and energy are conserved. The other productions $\Pi_\alpha (\alpha = 5, 6, \ldots n - 1)$ vanish in equilibrium. That property defines the equilibrium state. Further equations – for $n > 4$ – may have the heat flux and the stress as densities, or higher moments, or additional internal variables whatever they may be; and their productions do generally *not* vanish.

8.4.2 Constitutive theory. Symmetric hyperbolic systems

The most important tool of the constitutive theory is the entropy principle, believed in because of the arguments of Clausius and Boltzmann, see Section 2. The entropy principle of extended thermodynamics has two parts. The first one is the *entropy inequality*

$$\frac{\partial h}{\partial t} + \frac{\partial h_d}{\partial x_d} = \Sigma \geq 0 \qquad \text{for all thermodynamic processes.} \tag{8.19}$$

The entropy density h, entropy flux h_d and entropy production Σ are constitutive quantities of the type (8.17), i.e. local and instantaneous ones[72]

$$h = \hat{h}(u_\gamma), \qquad h^d = \hat{h}_d(u_\gamma), \qquad \Sigma = \hat{\Sigma}(u_\gamma). \tag{8.20}$$

The second part of the entropy principle is the requirement of concavity of the entropy density

$$\frac{\partial^2 h}{\partial u_\gamma \partial u_\beta} - \text{negative definite.} \tag{8.21}$$

This property allows the entropy to reach a maximum in equilibrium.

Another important ingredient of the constitutive theory is the frame indifference of the field equations under Galilean transformations. Its exploitation requires the knowledge of the tensorial character of the variables u_α and, since we have not specified that, frame indifference cannot be exploited here, at least not in the present synthetic scheme[73].

The key to the exploitation of the inequality (8.19) is the observation that the inequality must hold for all thermodynamic processes, i.e. solutions of the field equations. Thus, in a manner of speaking the field equations provide *constraints* on the fields for which the inequality must hold. It can be shown [Liu 1972a; 1972b] that we may get rid of those constraints with the use of Lagrange multipliers Λ_α. Indeed, the new inequality

$$\frac{\partial h}{\partial t} + \frac{\partial h_d}{\partial x_d} - \Lambda_\alpha \left(\frac{\partial u_\alpha}{\partial t} + \frac{\partial F_{d\alpha}}{\partial x_d} - \Pi_\alpha \right) \geq 0 \tag{8.22}$$

must hold for all fields $u_\alpha(x_i, t)$. The Λ_α's may be functions of the fields u_α. Insertion of the constitutive relations for h, h_d and $F_{d\alpha}$ and the application of the chain rule provides

$$\left(\frac{\partial h}{\partial u_\alpha} - \Lambda_\alpha \right) \frac{\partial u_\alpha}{\partial t} + \left(\frac{\partial h_d}{\partial u_\beta} - \Lambda_\alpha \frac{\partial F_{d\alpha}}{\partial u_\beta} \right) \frac{\partial u_\beta}{\partial x_d} + \Lambda_\alpha \Pi_\alpha \geq 0. \tag{8.23}$$

The left hand side is linear in the derivatives of u_α, and since the inequality must hold for all fields, it must hold in particular for arbitrary values of the derivatives $\frac{\partial u_\alpha}{\partial t}$ and $\frac{\partial u_\alpha}{\partial x_d}$ at one point and time. Hence follows

$$dh = \Lambda_\alpha du_\alpha, \qquad dh_d = \Lambda_\alpha dF_{d\alpha}, \qquad \text{and} \qquad \Sigma = \Lambda_\alpha \Pi_\alpha \geq 0, \tag{8.24}$$

lest the inequality should be violated.

These are the results of the entropy inequality and all of them contain the Lagrange multipliers which are auxiliary quantities. Even the entropic quantities h and h_d are auxiliary quantities in a manner of speaking because, after all, the constitutive theory has set out to find restrictions on the constitutive functions in (8.17) and h and h_d are supposed to help in that effort. Really useful results for our purpose should not contain the auxiliary quantities. But still, let us continue, because there will be some definite results without a specific characterisation of the densities, and without the knowledge of the Lagrange multipliers.

Differentiation of (8.24)$_1$ with respect to u_β shows that $\frac{\partial \Lambda_\alpha}{\partial u_\beta}$ is negative definite because of the assumed concavity of the entropy density h. Therefore, the Lagrange

multipliers Λ_α may serve as variables instead of u_α. If we introduce the scalar potential $h' = \Lambda_\alpha u_\alpha - h$ as the Legendre transform of h associated with the map $u_\alpha \Leftrightarrow \Lambda_\alpha$ and the vector potential $h'_d = \Lambda_\alpha F_{d\alpha} - h_d$, we obtain from (8.24)

$$dh' = u_\alpha d\Lambda_\alpha, \qquad dh'_d = F_{d\alpha} d\Lambda_\alpha, \quad \text{and} \quad \Sigma = \Lambda_\alpha \Pi_\alpha \geq 0 \text{ as before,} \qquad (8.25)$$

so that the densities and fluxes are seen to be derivatives of the potentials with respect to Λ_α. Note that h' is concave in the Lagrange multipliers, since h is concave in the densities, because a Legendre transformation does not affect the concavity.

Thus the field equations (8.16) may be expressed as

$$\frac{\partial^2 h'}{\partial \Lambda_\alpha \partial \Lambda_\beta} \frac{\partial \Lambda_\beta}{\partial t} + \frac{\partial^2 h'_d}{\partial \Lambda_\alpha \partial \Lambda_\beta} \frac{\partial \Lambda_\beta}{\partial x_d} = \Pi_\alpha. \qquad (8.26)$$

A system of differential equations like this – with symmetric matrices and a definite matrix for the temporal derivative $\frac{\partial \Lambda_\beta}{\partial t}$ – is called a symmetric hyperbolic system. Thus we conclude that the entropy principle guarantees that the field equations are symmetric hyperbolic when the Lagrange multipliers are used as the fields. Boillat has therefore called the Lagrange multipliers *privileged* fields, or *main* fields [Boillat 1974].

It is clear that Boillat did not know about Lagrange multipliers in 1974. However, he found the privileged fields and later Ruggeri and Strumia identified those fields with the Lagrange multipliers of extended thermodynamics. This was the moment when the mathematical theory of hyperbolic systems was joined to thermodynamics, or vice versa [Ruggeri 1981].

The fields Λ_α are called *privileged*, because symmetric hyperbolic systems have convenient and desirable properties, namely the well-posedness of initial value problems, i.e. existence and uniqueness of solutions and continuous dependence of solutions on the data, e.g. see [Godunov 1961][74] and [Fisher 1972]. Also symmetric hyperbolic systems imply finite speeds.

The ingredients of the formal structure of extended thermodynamics are not only mathematically desirable, they also please the physicist. The attractive features include

- field equations of balance type;
- local and instantaneous constitutive relations;
- existence of a non-equilibrium entropy density;
- general constitutive entropy flux;
- thermodynamic stability, well-posedness of initial value problems; and
- finite speeds.

If we assume that thermodynamics eventually should represent an integral part of mathematical physics, the foregoing analysis represents a large step forward: *the entropy principle has led to symmetric hyperbolic field equations.* We are tempted to postulate that all valid thermodynamic field theories ought to be of that type.

It remains to exploit the residual inequality (8.24)$_3$ for the entropy production density Σ, which is assumed non-negative and is obviously minimal, namely zero, in equilibrium, where all productions Π_α vanish. We may write

$$\Sigma = \sum_{\alpha=5}^{n-1} \Lambda_\alpha \Pi_\alpha,$$

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[74] Godunov found the proper variables for symmetric hyperbolicity of the field equations of Euler fluids.

since Π_α ($\alpha = 0, 1, \ldots 4$) are always zero, equilibrium or not[75]. Thus of necessity we have[76]

$$\left.\frac{\partial \Sigma}{\partial \Pi_\alpha}\right|_E = \Lambda_\alpha|_E = 0 \quad (\alpha = 5, 6 \ldots n - 1). \tag{8.27}$$

We conclude that the Lagrange multipliers Λ_α ($\alpha = 5, 6 \ldots n-1$) vanish in equilibrium. If the productions Π_α are assumed to be linear functions of Λ_α ($\alpha = 5, 6 \ldots n - 1$), we may write

$$\Pi_\alpha = \sum_{\beta=5}^{n-1} L_{\alpha\beta} \Lambda_\beta \quad (\alpha = 5, 6 \ldots n - 1) \tag{8.28}$$

and, obviously, the matrix $L_{\alpha\beta}$ ($\alpha, \beta = 5, 6 \ldots n-1$) must be positive definite, because of the inequality $(8.24)_3$, but it is not necessarily symmetric. We shall discuss the symmetry of $L_{\alpha\beta}$ in Section 9.5, where we consider the special case that the densities u_α are moments.

8.4.3 Wave speeds. Growth and decay of acceleration waves

A wave is defined as a propagating surface and mathematically it is represented by the equation $\varphi(x_i, t) = 0$. Its normal n_i and normal speed V are given by

$$n_i = \frac{\frac{\partial \varphi}{\partial x_i}}{|\text{grad } \varphi|} \quad \text{and} \quad V = -\frac{\frac{\partial \varphi}{\partial t}}{|\text{grad } \varphi|}.$$

Here we are interested in weak waves[77], surfaces across which the fields u_α, or Λ_α, are continuous although their gradients are not. Obviously the jump of the gradient of Λ_α must then point in the normal direction which we may take to be the 1-direction. Therefore we have

$$\left[\frac{\partial \Lambda_\alpha}{\partial x_1}\right] = A_\alpha \quad \text{and} \quad \left[\frac{\partial \Lambda_\alpha}{\partial t}\right] = -V A_\alpha; \tag{8.29}$$

square brackets indicate differences between the two sides of the wave. Thus from the field equations (8.26) we obtain a linear homogeneous algebraic system for the A_α's, viz.

$$\left(\frac{\partial^2 h_1'}{\partial \Lambda_\alpha \partial \Lambda_\beta} - \frac{\partial^2 h'}{\partial \Lambda_\alpha \partial \Lambda_\beta} V\right) A_\alpha = 0 \quad \text{or, equivalently}$$

$$\left(\left(\frac{\partial^2 h'}{\partial \Lambda_\alpha \partial \Lambda_\gamma}\right)^{-1} \frac{\partial^2 h_1'}{\partial \Lambda_\gamma \partial \Lambda_\beta} - V \delta_{\alpha\beta}\right) A_\alpha = 0. \tag{8.30}$$

It follows that the jumps of the gradients are proportional to the right eigenvalues d_α of the matrix in $(8.30)_2$. We may then write $A_\alpha = A d_\alpha$, and call A the *amplitude* of the wave. Therefore the possible speeds – called characteristic speeds – are the

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[75] Normally the summation over the repeated index α is understood. But here we write the sum explicitly so as to be able to indicate that it extends over $\alpha = 5, 6 \ldots n - 1$ only rather than over all α from 0 through $n - 1$.

[76] For once we take the productions as the variables, – instead of the densities or Lagrange multpliers – under the weak assumption that this is possible.

[77] Also called acceleration waves – mostly in fluid mechanics – because the velocity is continuous, but the acceleration is not.

roots of an nth order algebraic system that results from setting the determinant of the system equal to zero

$$\det\left(\left(\frac{\partial^2 h'}{\partial \Lambda_\alpha \partial \Lambda_\gamma}\right)^{-1}\frac{\partial^2 h'_1}{\partial \Lambda_\gamma \partial \Lambda_\beta} - V\delta_{\alpha\beta}\right) = 0. \tag{8.31}$$

There are n such speeds, in other words we have n *sounds*. But, of course, we cannot calculate any of them before knowing h' and h'_1 as functions of Λ_α; see Section 9. We only know that the V's following from (8.31) are real and finite; we know that from the symmetric hyperbolic character of the field equations.

The amplitude may decay or it may grow depending on its initial value and on the size of the production terms Π_α, that represent dissipation, and on the non-linearity, i.e. the dependence of V on the fields. In the case of propagation into an unperturbed state of equilibrium the governing equation for the rate of change of the amplitude A is a Bernoulli equation

$$\frac{\delta A}{\delta t} \underbrace{- \frac{\partial V}{\partial u_\beta}d_\beta}_{\alpha\text{-nonlinearity}}A^2 \underbrace{- l_\alpha\frac{\partial \Pi_\alpha}{\partial u_\gamma}d_\gamma}_{\beta\text{-dissipation}}A = 0 \quad \text{with the solution}$$

$$A(t) = \frac{A(0)\exp\left[-\beta t\right]}{1 - A(0)\frac{\alpha}{\beta}\left(\exp\left[-\beta t\right] - 1\right)}. \tag{8.32}$$

d_α and l_α are the right and left eigenvectors of the matrix in (8.30)$_2$.

It seems that the first person to calculate the rate of change of the amplitude of an acceleration wave was Green [Green 1964]. The elegant form (8.32)$_1$ of the Bernoulli equation is due to Boillat again, the discoverer of the privileged fields [Boillat 1965]. An instructive review on waves – in particular acceleration waves – is given by Chen [Chen 1973].

The non-linearity in (8.32) occurs, if the wave velocity depends on the value of the fields u_β, – as it does for a breaking water wave. Inspection of (8.32) shows that without the non-linearity, i.e. for $\alpha = 0$, the amplitudes decay exponentially. On the other hand, if we have $\alpha \neq 0$ and if β is sufficiently small and the amplitude $A(0)$ sufficiently large, there may be a blow-up: at time

$$t_{cr} = \frac{1}{\beta}\ln\frac{1}{1 + \frac{\beta}{\alpha}\frac{1}{A(0)}} \tag{8.33}$$

the amplitude of the acceleration wave becomes infinite and that means that the velocity has a jump; we may say that the acceleration wave has then grown into a *shock wave*. We see from (8.33) that this can only happen for $|A(0)| > \frac{\beta}{\alpha}$, meaning that the initial amplitude is too big to be damped in the course of time.

8.4.4 Natura non fecit saltus[78]

Nature does not admit jumps. Indeed, experiments show that shocks as discontinuities of the velocity field do not exist; rather shock waves represent smooth albeit steep

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[78] Aristoteles said it in Greek, of course, and in his "History of animals", which means that he was not speaking of shocks. However, the familiar quote is often used in connection with shocks and shock structures.

decreases of velocity, so-called shock structures. Therefore, if a symmetric hyperbolic system predicts a singular amplitude of an acceleration wave, as explained in Section 8.4.3, we know that the system is inappropriate to describe nature. Usually in that situation we must extend the theory by taking additional variables into account, and thus adding more dissipation. In the next chapter we shall encounter examples. Extended thermodynamics of moments is well-equipped for dealing with the situation, because *extension* is its *raison d'être*.

Also, in the next chapter we shall explain why – under the right set of circumstances – it may be useful to simulate a continuous but steep field as an actual jump, even though jumps are unphysical, see Section 9.6.

9 Extended thermodynamics of moments

9.1 Abstract

The foregoing synthetic formal structure of extended thermodynamics describes a general framework to be supplemented by a specific choice of variables u_α. In the present chapter we let us be guided by the kinetic theory of gases and choose moments of the distribution function as variables. Indeed, the kinetic theory of monatomic gases provides a structure that fits perfectly well into the structure of extended thermodynamics; it represents a special case.

For that special case we obtain specific results: the speeds of propagation may be calculated explicitly, and they turn out to be finite, of course, and growing with the tensorial rank of the moments which are drawn into the theory. Experimental results on light scattering in a rarefied gas can be verified in a most satisfactory manner. The calculation of shock structures reveals an interesting role played by the pulse speeds of the governing symmetric hyperbolic system. Also there is an interesting symmetry relation between productions and Lagrange multipliers which provides a possible reinterpretation of Onsager's symmetry relation.

9.2 Moments as variables

The kinetic theory of gases suggests a particularly simple special case for which the tenets of extended thermodynamics are satisfied. Thus the kinetic theory with its balance equations (7.12) for moments provides an example for the generic system

$$\frac{\partial u_\alpha}{\partial t} + \frac{\partial F_{i\alpha}}{\partial x_i} = \Pi_\alpha, \tag{9.1}$$

which we have assumed as the basis of extended thermodynamics. Comparison leads us to set

$$u_\alpha = \mu \int c_\alpha f dc \quad \text{where} \quad c_\alpha = 1 \qquad \text{for } \alpha = 0$$

$$F_{i\alpha} = \mu \int c_i c_\alpha f dc \qquad c_\alpha = \begin{vmatrix} c_{i_1} \\ c_{i_1} c_{i_2} \\ \bullet \\ \bullet \\ c_{i_1} c_{i_2} \dots c_{i_N} \end{vmatrix} \qquad \text{for } \alpha = 1, 2, \dots n-1$$

$$\Pi_\alpha = \mu \int c_\alpha S(f) dc \tag{9.2}$$

so that the densities and fluxes are *both* moments of the distribution function and the productions are moments of the collision term in the Boltzmann equation[79]. What makes the case special is the fact that the densities in one equation are equal to the fluxes in the foregoing equation. In this manner only one flux of rank $N + 1$, namely $F_{i\,i_1 i_2...i_N}$, is needed for closure and, in addition, the productions for $n > 4$. We assume that all of those are functions of the densities u_α ($\alpha = 0, 1, 2 \ldots n - 1$) as they would be if we used Grad's closure, see Section 7. Also, according to Section 7.4 the kinetic theory provides an entropy inequality with a concave entropy density. Thus all the basic ingredients of extended thermodynamics are available in the theory of moments, and therefore we may transfer the results of extended thermodynamics to the moment theory.

In particular, the results (8.25) concerning the scalar and vector potential now read

$$dh' = u_\alpha d\Lambda_\alpha = \mu \int f d (\Lambda_\alpha c_\alpha) \, dc = \mu \int dF (\Lambda_\alpha c_\alpha) \, dc = d \left(\mu \int F (\Lambda_\alpha c_\alpha) \, dc \right)$$

$$dh'_i = F_{i\alpha} d\Lambda_\alpha = \mu \int c_i f d (\Lambda_\alpha c_\alpha) \, dc = \mu \int c_i dF (\Lambda_\alpha c_\alpha) \, dc = d \left(\mu \int c_i F (\Lambda_\alpha c_\alpha) \, dc \right).$$
$$(9.3)$$

By the second and third step in those two strings of equations f and F are functions of the single variable $\chi = \Lambda_\alpha c_\alpha$ and the distribution function f is the derivative of F with respect to that variable.

It follows that we have – to within constants that we may ignore –

$$h' = \mu \int F (\chi) \, dc \qquad h'_i = \mu \int c_i F (\chi) \, dc, \qquad \text{where} \qquad F' = f \qquad (9.4)$$

so that the symmetric hyperbolic system (8.26) reads

$$\mu \int c_\alpha c_\beta f' dc \frac{\partial \Lambda_\beta}{\partial t} + \mu \int c_i c_\alpha c_\beta f' dc \frac{\partial \Lambda_\beta}{\partial x_i} = \Pi_\alpha. \qquad (9.5)$$

In extended thermodynamics of moments the distribution function can be determined from the knowledge of the entropy density $(7.17)_1$: in order to see that we recall the definitions of the potentials

$$h' = \Lambda_\alpha u_\alpha - h \qquad \text{and} \qquad h'_i = \Lambda_\alpha F_{i\alpha} - h_i \qquad (9.6)$$

and obtain the entropy density and entropy flux from (9.4)

$$h = \mu \int (\chi F' - F) \, dc \qquad \text{and} \qquad h_i = \mu \int c_i (\chi F' - F) \, dc. \qquad (9.7)$$

Comparison of $(9.7)_1$ with the kinetic definition $(7.17)_1$ of the entropy density identifies the distribution function as an exponential function

$$f = y \exp \left[-\frac{\Lambda_\alpha c_\alpha}{k/\mu} \right], \qquad \text{hence} \qquad f' = -\frac{1}{k/\mu} f. \qquad (9.8)$$

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[79] Among the densities we include moments up to tensorial rank N with all their components. In that case the symmetry of the moments implies that we have $n = 1/6(N + 1)(N + 2)(N + 3)$ densities and the field equations are 1, 4, 10, 20, 35, 56, ... in number. Note that the otherwise attractive 13-moments theory is not in this hierarchy, because it accepts the trace of the third moments F_{ijj} among the variables and ignores its traceless part $F_{\langle ijk \rangle}$.

Thus, in a manner of speaking the system is now closed, because from the knowledge of f the flux $F_{i\,i_1 i_2 \ldots i_N}$ and the productions Π_α – see (7.11) – can be determined in terms of the Λ_α's, at least in principle

$$F_{i\,i_1 i_2 \ldots i_N} = \mu y \int c_i c_{i_1} \ldots c_{i_N} \exp\left[-\frac{\Lambda_\alpha c_\alpha}{k/\mu}\right] dc \qquad \text{and}$$

$$\Pi_\alpha = \frac{1}{4}\mu y^2 \int \left(c_\alpha + c_\alpha^1 - c_\alpha' - c_\alpha^{1'}\right)\left(\exp\left[-\frac{\Lambda_\beta\left(c_\beta' + c_\beta^{1'}\right)}{k/\mu}\right] - \exp\left[-\frac{\Lambda_\beta\left(c_\beta - c_\beta^1\right)}{k/\mu}\right]\right)$$

$$\times \, rV \sin\Theta d\Theta d\varepsilon \, dc dc^1. \tag{9.9}$$

There is a catch though, because the variables here are the Lagrange multipliers Λ_α, and not the densities u_α. It is true, in principle we may calculate the Lagrange multipliers from the densities by

$$u_\alpha = \mu \int c_\alpha y \exp\left[-\frac{\Lambda_\alpha c_\alpha}{k/\mu} dc\right], \tag{9.10}$$

but this cannot be done analytically, or only in an approximate manner, and exactly only in equilibrium.

Indeed, in equilibrium we have $\Lambda_\alpha|_E = 0$ for $(\alpha = 5, 6, \ldots n - 1)$, see (8.27), and the first five moments are ρ, ρv_i, $2\rho(u + \frac{1}{2}v^2)$ so that (9.10) implies

$$\Lambda_0|_E = \frac{v^2}{2T} - \frac{g|_E}{T}, \qquad \Lambda_j|_E = -\frac{v_j}{T}, \qquad \Lambda_4|_E = -\frac{1}{2T}, \tag{9.11}$$

where u has been replaced by $\frac{3}{2}{}^{k/\mu}T$, see (7.10). Also $g|_E = u + \frac{p}{\rho} - Ts|_E$ is the specific Gibbs free energy, often called chemical potential. Thus in equilibrium the distribution function is reduced to the Maxwell distribution (7.18) which may also be written as

$$f_E = y \exp\left[-\frac{g_E + \frac{1}{2}\left(c_i - v_i\right)^2}{k/\mu T}\right]. \tag{9.12}$$

As a corollary of (9.4) and (9.8) we obtain $h' = -{}^{k/\mu}\rho$ and $h'_i = -{}^{k/\mu}\rho v_i$ so that we have

$$u_\alpha \frac{\partial \Lambda_\alpha}{\partial t} + F_{i\alpha} \frac{\partial \Lambda_\alpha}{\partial x_i} = 0. \tag{9.13}$$

This equation is equivalent to the conservation law of mass written here in terms of the Lagrange multipliers. In order to identify the status of the equation we calculate it for the special case of an Euler fluid, see Figure 14, where the deviatoric stress and the heat flux are ignored so that the fluid is always locally and instantaneously in equilibrium. In that case equation (9.13) reduces to the Gibbs equation which may be written as

$$\rho \frac{d\left(-\frac{g|_E}{T}\right)}{dt} + \frac{d\left(\frac{p}{T}\right)}{dt} + u\frac{d\left(\frac{1}{T}\right)}{dt} = 0 \quad \text{or} \quad m\frac{d\left(-\frac{g|_E}{T}\right)}{dt} + V\frac{d\left(\frac{p}{T}\right)}{dt} + U\frac{d\left(\frac{1}{T}\right)}{dt} = 0. \tag{9.14}$$

Thus (9.13) may be called the extension of the Gibbs equation appropriate for non-equilibrium and, of course discussed here for moments only. It is not surprising, perhaps, that this is a partial differential equation rather than the ordinary differential equation valid in equilibrium. One might be tempted to extrapolate (9.13) away

from monatomic ideal gases but that would be no more than speculation, tempting but precarious, although permissible – perhaps – as a heuristic measure.

One more observation concerning $(9.14)_2$: it is often said that the Gibbs equation, – particularly in its form $(9.14)_2$ – provides a relation between *extensive* variables, viz. m, V, U and their *conjugate intensive* variables, viz. g, p, and T. Personally, we have never found that classification useful for anything. However, maybe in the extension (9.13) of the Gibbs equation it may help to interpret the privileged field: we might, perhaps, be motivated by the distinction to call the densities u_α extensive and the corresponding Lagrange multipliers Λ_α intensive. The latter's rates of change and gradients are orthogonal to the $4n$-vector $\{u_\alpha, F_{i\alpha}\}$ in the vector space spanned by the densities and their fluxes.

9.3 Speeds of characteristic waves

Conceptually it is now nearly trivial – for a properly programmed computer – to calculate the characteristic speeds of the multifarious modes of sound in a monatomic gas, at least, if the sound propagates into a region of undisturbed equilibrium. In that case the matrices of the symmetric hyperbolic system (8.26) or (9.5) may be calculated from the Maxwell distribution; its elements are Gauss integrals of the type $\int x^n \exp[-x^2]dx$. Therefore the algebraic equation (8.31) can be solved to provide the characteristic speeds V. Weiss has focused the attention on longitudinal waves and has calculated their speeds for many values of N [Weiss 1990]. His results are summarised in Figure 16. In diagram (a) of the figure we see all speeds V up to $N = 43$; some are smaller than the ordinary low-frequency sound speed $v_0 = \sqrt{\frac{5}{3}\frac{k}{\mu}T}$, but most are bigger. The largest characteristic speed, the pulse speed $V^{\max}$, is listed in the table of Figure 16. It grows with N, the highest tensorial rank of the moments in the theory and that growth may be read off from the crosses in diagram (b). The table also shows the number of longitudinal waves corresponding to N: for $N = 10$ there are 286 speeds and 36 of them are longitudinal; for $N = 30$ those numbers rise to 5456 and 256 respectively. Only one of all those waves can actually be *heard*, since all others are strongly damped. The one mode that can be heard is the one whose low-frequency phase speed is v_0, our usual sound speed. The situation is akin to the two sound modes in a mixture, see Section 6.4, where the second sound was strongly damped under normal conditions; in that case there *were* only *two* sounds.

Clearly from Figure 16 the suspicion arises that for $N \to \infty$ the pulse speed grows indefinitely and that was indeed proved by Boillat and Ruggeri [Boillat 1997], see also [Müller 1998]. In an ingenious estimate the authors found a lower bound of $V^{\max}$, namely

$$V^{\max} \geq \sqrt{\frac{6}{5}\left(N + \frac{1}{2}\right)}, \tag{9.15}$$

so that for $N \to \infty$ the pulse speed $V^{\max}$ indeed tends to infinity. In diagram (b) of Figure 16 the dots represent the lower bound.

This result seems to represent some kind of anticlimax for a theory which originally had set out to calculate finite speeds and thus avoid paradoxes. However, we consider $V^{\max} \xrightarrow[N \to \infty]{} \infty$ as an artifact created by the definition of the moments in which the distribution function represents atoms of speeds of any size. Anyway, for finitely many equations all moment theories of extended thermodynamics have finite speeds. Incidentally, in a relativistic theory of many moments the limiting speed is c, the speed of light, rather than infinity, which is as it should be [Boillat 1997; Müller 1999].

| n	longitudinal waves	N	V^{max}/v_0
4	2	1	0.77459667
10	4	2	1.34164079
20	6	3	1.80822948
35	9	4	2.21299946
56	12	5	2.57495874
84	16	6	2.90607811
120	20	7	3.21035245
165	25	8	3.49555791
220	30	9	3.76412372
286	36	10	4.01860847
364	42	11	4.26098014
455	49	12	4.49279023
560	56	13	4.71528716
680	64	14	4.92949284
816	72	15	5.13625617
969	81	16	5.3362913
1140	90	17	5.53020569
1330	100	18	5.71852112
1540	110	19	5.90166962
1771	121	20	6.08010585
2024	132	21	6.25411673
2300	144	22	6.42402919
2600	156	23	6.59011627
2925	169	24	6.75262213
3276	182	25	6.91176615
3654	196	26	7.06774831
4060	210	27	7.22074198
4495	225	28	7.37091629
4960	240	29	7.51841807
5456	256	30	7.66333382
5984	272	31	7.80593804
6545	289	32	7.94619654
7140	306	33	8.08426549
7770	324	34	8.22024331
8436	342	35	8.35422129
9139	361	36	8.48628432
9880	380	37	8.61651144
10660	400	38	8.74497544
11480	420	39	8.87174833
12341	441	40	8.99689171
13244	462	41	9.12046722
14190	484	42	9.24253184
15180	506	43	9.36313918
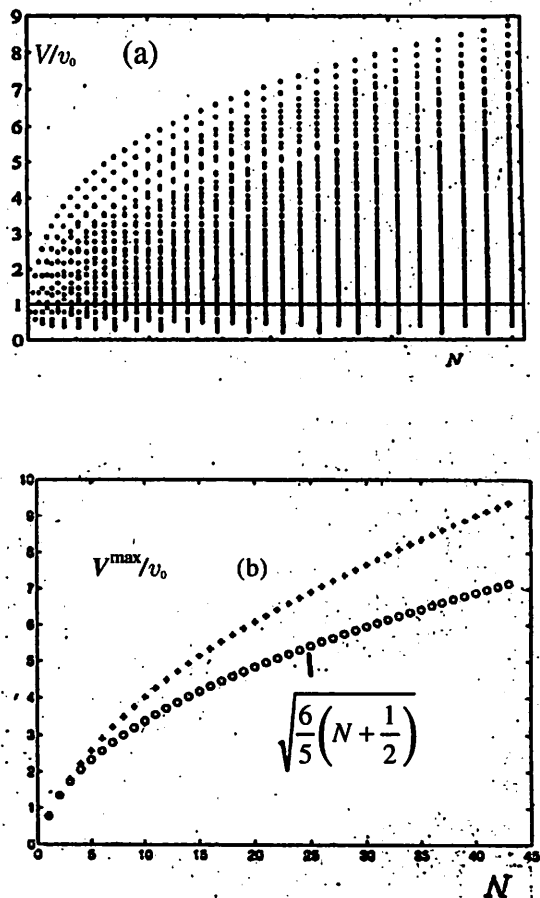
Fig. 16. Characteristic speeds. Table: pulse speed as function of n and N. (a) Characteristic speeds for a chosen N. (b) Pulse speed as function of N. Crosses: calculation. Circles: lower bound.

9.4 Light scattering

Light scattering is a paradigm for the usefulness and practicality of extended thermodynamics and, in particular, of extended thermodynamics of moments. Let us consider this.

Incoming laser light, i.e. light of a single frequency ω_i, – most often green light with the wave length $\lambda_i \approx 0.4 \times 10^{-6}$ m – is scattered on the density fluctuations of a gas in equilibrium, see Figure 17a. While most of the scattered light has the same frequency as the incoming light, the scattering spectrum also contains neighbouring frequencies. For a dense gas – typically a gas under a pressure of 4 bar – the spectrum has three well-pronounced peaks, like the uppermost curve in Figure 17b. When that gas pressure is lowered, the peaks become less pronounced; they degenerate into *shoulders*, until eventually – for pressures much less than 1 bar – there is a single *bump* in the middle.

As long as there are peaks, i.e. for dense gases, the distance of the central and lateral peaks determines the sound speed of the gas, or its temperature. From the half-width of the peaks and their relative height we may read off the viscosity and thermal conductivity of the gas. That should come as a surprise! Indeed, we may well ask a question: How, if the scattering spectrum represents properties of density fluctuations in equilibrium, can it carry information about macroscopic transport coefficients like the viscosity η?
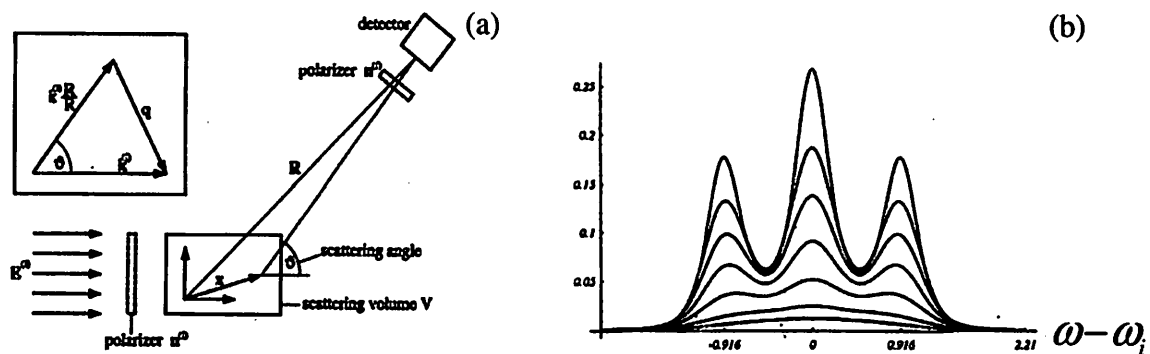
Fig. 17. Light Scattering and scattering spectrum. (a) Schematic experimental set-up. (b) Experimental curves [Au 1997].

For an answer, it is not unimportant to know what the scattering spectrum consists of. The scattered light reaching the detector is an amplitude-modulated oscillation with the basic frequency ω_i. The amplitude modulation is provided by the density fluctuation $\delta\rho(r_n, t)$ in all points $r_n \in V$, but only through its spatial Fourier harmonic $\delta\rho(q_n, t)$ with the wave number $q_n = k_n^i - \frac{\omega_i}{c}\frac{R_n}{R}$ (see the vector triangle in the inset of Fig. 17a) so that forward scattering, with $\vartheta \ll \pi$, represents large-scale density fluctuations and backward scattering with $\vartheta \lesssim \pi$ is created by small-scale fluctuations. It is a considerable achievement of experimental optics that a Fabry-Perot interferometer detects the *mean regression* of the fluctuating amplitude modulation, or rather its *auto-correlation* function, which is the mean value of mean regressions, averaged over all fluctuation sizes. More precisely, the Fabry-Perot interferometer registers the temporal Fourier component of the auto-correlation function[80]. This is a function of ω which we have loosely called scattering spectrum in describing Figure 17b, and we shall continue to do so[81].

The proper measure for the degree of rarefaction is given by the dimensionless quantity $y = p(\frac{k}{\mu}T)^{-1/2}\frac{1}{\eta}\frac{1}{q}$ so that the same scattering spectrum is expected for large scattering angle and low pressure p, or for forward scattering and high pressure. It is easier to change the pressure in the scattering chamber than the position of the detector. Therefore experimental data, like those of Figure 17b are usually acquired by varying the pressure of the gas.

Now, we recall that we have met mean regression functions before, namely in Section 3, where we have discussed the Onsager theory. According to Onsager's hypothesis the mean regression of a fluctuation - here the fluctuation of the spatial Fourier harmonic of the density fluctuation - behaves like a macroscopic relaxation, - here the relaxation of the spatial Fourier harmonic of a density disturbance. The latter may be calculated by a macroscopic theory, e.g. the Navier-Stokes theory or extended thermodynamics.

Thus we may *calculate* scattering spectra in a dense gas by a simple recipe as follows:

- write the Navier-Stokes equations;
- make a spatial Fourier transformation;
- solve the resulting system of rate laws - i.e. ordinary differential equations in time - for the density harmonic by use of a Laplace transformation; and
- average over initial conditions.

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[80] A detailed description of the Fabry-Perot interferometer may be found in the paper by Simonsohn [Simonsohn 1972]. A shorter version, appropriate to the present application, may be found in [Weiss 1995b].

[81] The proper name in the light-scattering literature is *dynamic form factor*.

$$S(\omega)$$

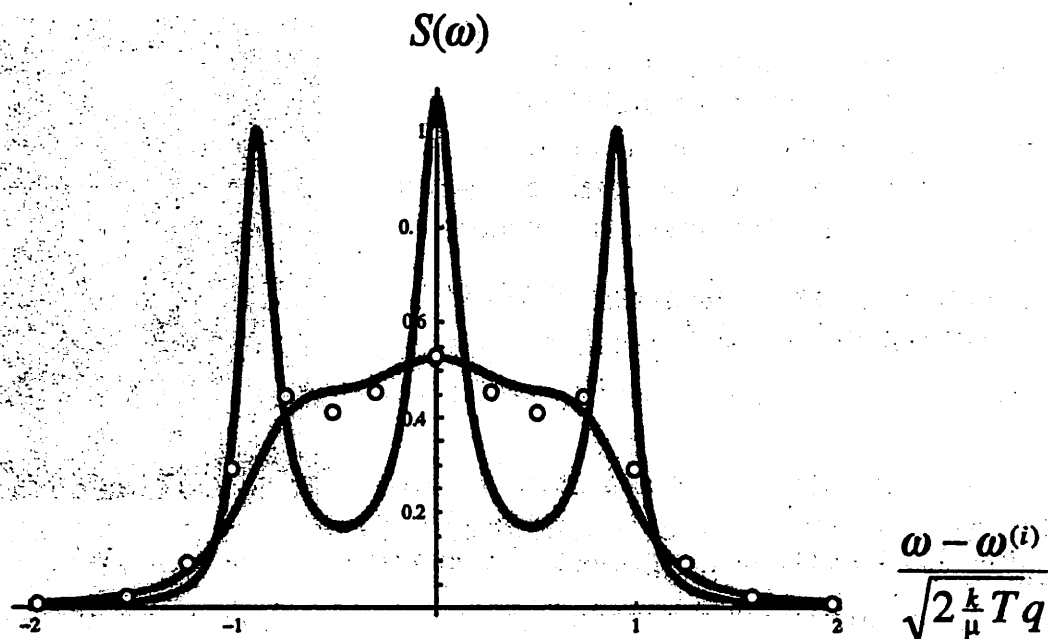$$\frac{\omega - \omega^{(i)}}{\sqrt{2\frac{k}{\mu}Tq}}$$

Fig. 18. Graphs: predicted scattering spectrum in a dense gas and a rarefied gas according to the Navier-Stokes-Fourier theory. Dots: measurements by Clark in rarefied xenon.

It is after the second step in this sequence where the Onsager hypothesis makes the connection between fluctuations and macroscopic relaxations. The fluctuating quantity is the spatial Fourier harmonic of a fluctuation.

So, if Onsager's hypothesis is correct, the analysis should provide the same scattering spectrum which is produced by the detector.

If we compare the experimental results for a *dense* gas with the result of this mathematical analysis of the Navier-Stokes-Fourier equations we obtain excellent agreement. Moreover, the transport coefficients so determined agree well with the values of viscosity and thermal conductivity measured by different means, or calculated from the kinetic theory of gases. This, of course, means no more and no less than that *the Onsager hypothesis on mean regression is supported by light scattering experiments.*

However, for a *rarefied* gas the agreement is not good, if we still use the Navier-Stokes equations. It is true that the expected gross features do appear: for a stronger degree of rarefaction the three peaks of the spectrum degenerate into shoulders and, eventually, into a bump, in the manner of Figure 17b. But the finer details are all wrong. The graphs in Figure 18 show the predictions of the mathematical analysis for dense xenon at 4 bar and for the same gas at 1 bar. The former graph, the one with the well pronounced peaks, fits observations perfectly well, but the graph for the rarefied gas obviously does not, because the dots represent observations made by Clark in xenon at one bar [Clark 1975]. Inspection shows considerable disagreement between experiment and calculation. We conclude from this observation that the Navier-Stokes theory is not valid in the rarefied gas. We consider this as an opportunity to check out the validity of the equations of extended thermodynamics of moments.

A prototypical case for the linearised equations of extended thermodynamics is the 20-moment system shown in Figure 14 and used there illustratively for the identification of various special cases. Weiss has the corresponding equations for any number of moments ready in the computer at the touch of a button and he has used them for the calculation of scattering spectra for $n = 20, 35, 56, 84$ in xenon for the
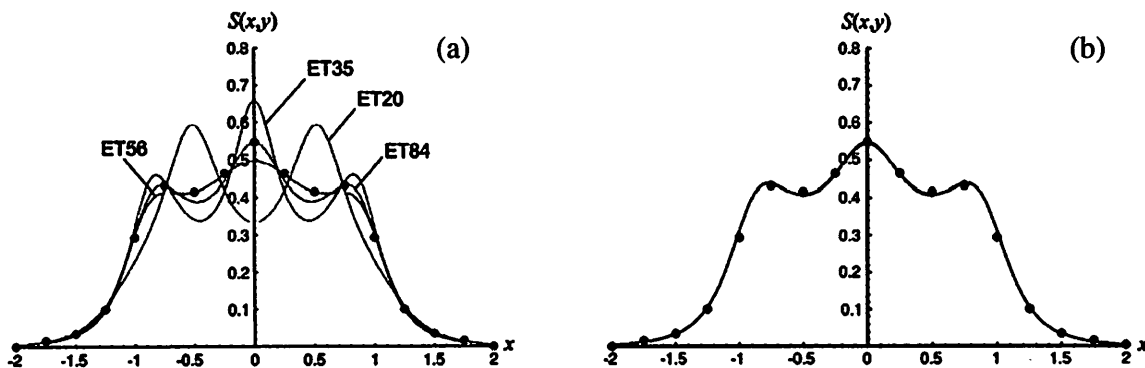
Fig. 19. Scattering spectra for xenon in extended thermodynamics. Dots represent measurements by Clark. (a) Spectra for 20, 35, 56, 84 moments. (b) Spectra for 120, 165, 220, 286 moments. All coincide to the naked eye.

rarefied conditions under which Clark's measurements were made. The results are shown in Figure 19a: Not two of them agree and none of them agrees with Clark's measured dots.

Ordinarily a situation like this calls for an adjustment of parameters, but that is impossible in the present case, because extended thermodynamics of moments is free of parameters. Indeed, in a manner of speaking extended thermodynamics is a theory of theories with only *one* parameter: *the number of equations*. So, Weiss has pushed that number to $n = 120$, 165, 220, and 286 and he obtained convergence of results at $n = 120$ in the sense that more moments do not change the scattering spectrum significantly and – what is more – they all agree with Clark's measured data, see Figure 19b for 1 bar. The same type of convergence happens at other pressures albeit, of course, for a different value of n.

In other words, for a given pressure our *theory of theories* provides the possibility to determine its own range of validity, something that is usually said a theory cannot possibly do. Here, if we have two successive theories which provide the same result, the lower one is good enough; and we may say this without conducting *a single experiment*!

All of this is most satisfactory, but there is also disappointment. Indeed, one might have hoped that 13 or 14 moments might bring about a great improvement over the Navier-Stokes-Fourier solution, and a good representation of experimental results. Instead we need hundreds of moments for even moderately rarefied gases. Although this may be disappointing, it is what nature requires.

For lower pressures we need even more moments. Indeed in a strongly rarefied gas even 210, or 256-moment theories still disagree, although their disagreement is kept to a narrow band (see Fig. 20). Inside this band runs a Gaussian distribution which is the ultimate scattering spectrum for the case $p \to 0$ and it reflects the Maxwellian distribution of the gas. This can be proved analytically, e.g. see [Weiss 1995b].

9.5 Shock waves

The best known phenomenon among all processes with steep gradients and rapid rates of change are shock structures, smooth but steep fields of density, velocity, and temperature (say). Observations show that the thickness δ of shock structures is not well represented by the Navier-Stokes-Fourier theory, see [Gilbarg 1953]. δ comes out too small compared to experiments by Alsmeyer, particularly at intermediate Mach numbers M_0 [Alsmeyer 1976], see Figure 21. Therefore, it is natural to try extended
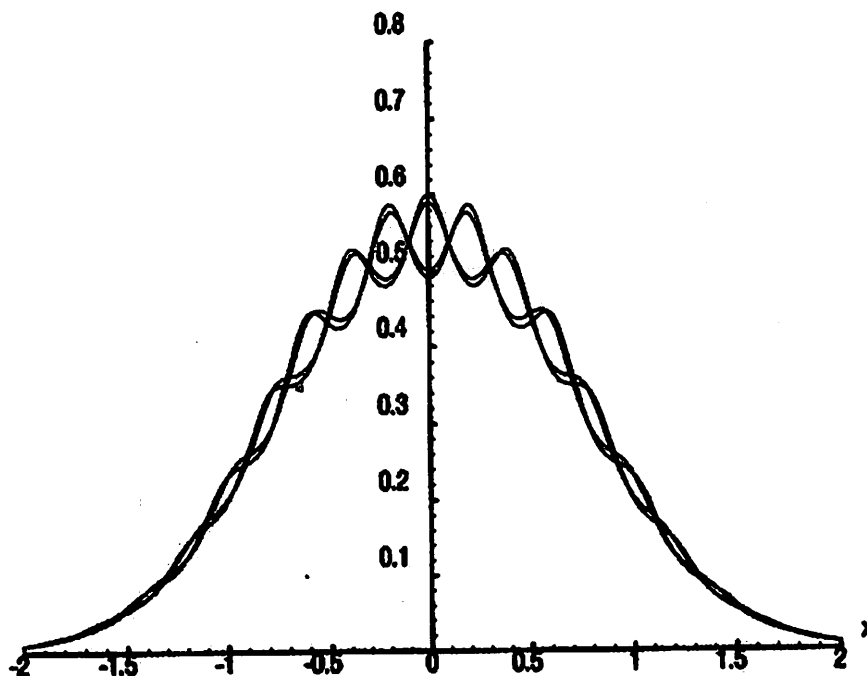
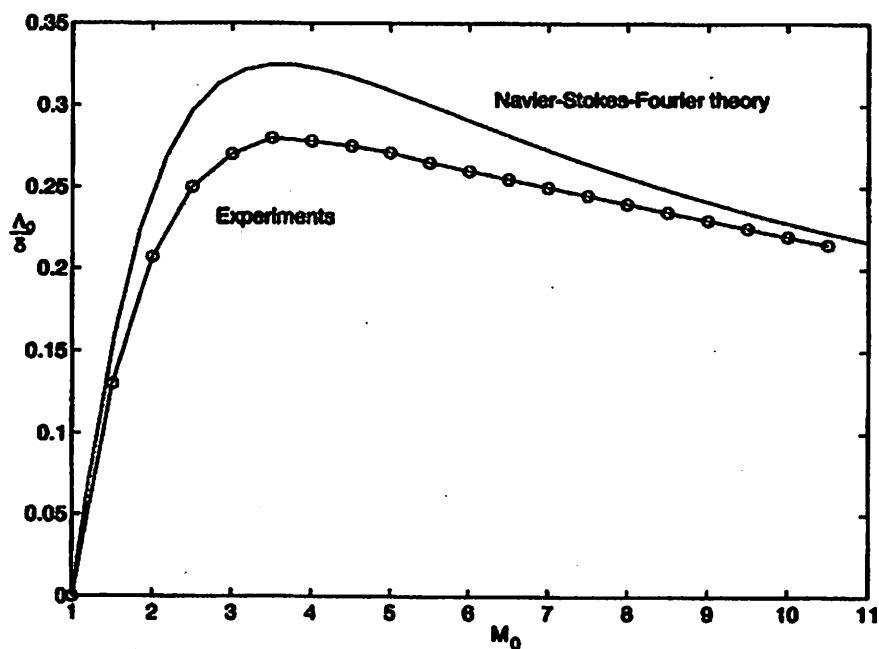**Fig. 20.** Scattering spectra at very low pressure. Calculations from moment theories between $n = 210$ through 256.

Fig. 21. Shock wave thickness δ in argon as a function of Mach number M_0. Λ_0 is the mean free path.

thermodynamics; after all, we have argued that extended thermodynamics is indicated for steep and fast processes.

The treatment of shock structures, however, is substantially more difficult with extended thermodynamics than the treatment of light scattering, because linearisation is impossible. Therefore to this day the discrepancy between theory and observation, put in evidence by Figure 21, has not been resolved; and not for lack of trying.
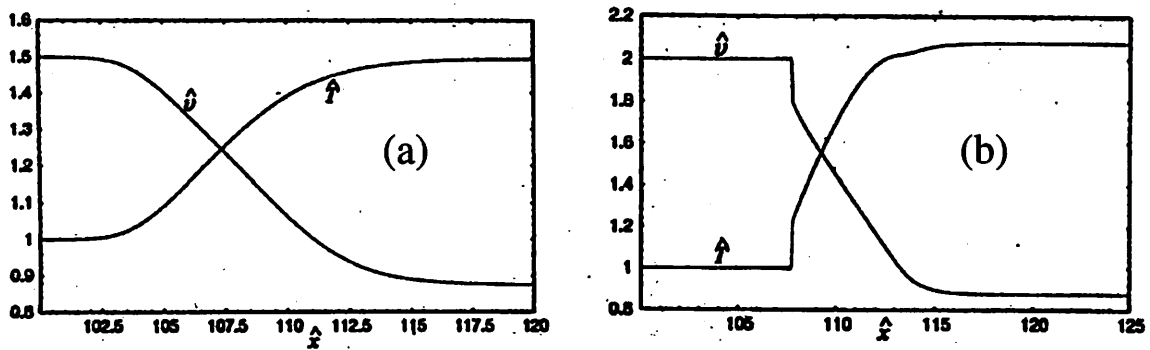
Fig. 22. (a) Smooth shock structure for $M_0 = 1.5$ in 13-moment theory. (b) Sub-shock for $M_0 = 2.0$.

Grad was well aware of the discrepancy, and when he invented the 13-moment theory (see Sect. 7) one of the first things he thought of for application was shocks [Grad 1957]. Maybe, he must have thought, he could do better than Navier-Stokes-Fourier. As it was, however, he came out worse, much worse! Let us consider the problem.

When Grad calculated the shock structure for $M_0 = 1.5$, – specifically the fields of velocity and temperature –, he obtained a perfectly reasonable result: smooth but steep shock structures (see Fig. 22a). That Mach number, i.e. $M_0 = 1.5$, was too small, however, to allow a definite conclusion about the shock thickness in comparison with the Navier-Stokes Fourier theory. Therefore Grad proceeded to $M_0 = 2.0$ and came up with a surprise: a sub-shock had appeared in both fields – see Fig. 22b – in stark contrast to experiments, which show smooth structures for all Mach numbers. That sub-shock in Grad's calculations starts out small at $M_0 = 1.65$ and grows with increasing Mach number. It is uncertain whether Grad recognised the significance of the number 1.65, – he does not say –, but the careful reader of this report will recall that in the 13-moment theory the pulse speed, – the greatest characteristic speed –, lies at $M_0 = 1.65$ (see Sect. 7.10). Therefore the reason for the appearance of the sub-shock is obvious: When the gas rushes toward the shock with a velocity greater than the pulse speed, there is nothing to prepare it, because the information about the approaching shock cannot reach the upstream region of the gas. In a manner of speaking only flows with $M_0 > 1.65$ are *truely supersonic* according to the 13-moment theory.

Once this was recognised it became clear that we must proceed to more moments, if we wish to avoid sub-shocks. After all, we have seen that the pulse speed increases with the number of moments (see the table in Fig. 16). And indeed, Weiss showed that in a 20-moment theory the subshock at $M_0 > 1.65$ has vanished only to reappear at $M_0 = 1.808$, the pulse speed for 20 moments; see table again [Weiss 1995a].

This is now understood. However, in order to push the incipient sub-shock as far as $M_0 = 9$ (say), we need a 12.341-moment theory according to the table in Figure 16, and that system of non-linear equations is so complex that no shock thickness could be calculated so far. Nor is the incentive very great, because in the meantime Bird has used molecular dynamics via Monte Carlo calculations to obtain perfectly realistic shock structures [Bird 1970].

A bizarre event happened at the time when Grad was stymied by sub-shocks: Holway published a paper in which he believed that he proved that the moment method could never allow smooth structures beyond $M_0 = 1.851$ [Holway 1964]. This was nonsense. At some point in his calculations Holway had confused the upstream and the downstream region of the shock. Weiss found and corrected the mistake [Weiss 1996b].

9.6 Jumps as a useful recipe

It is true that there are no jumps in nature nor any sub-shocks of the type shown in Figure 22b. Careful experimentation, as in the work reported by Alsmeyer confirms this statement [Alsmeyer 1976]. Extended thermodynamics of many moments – very many moments – or Monte Carlo calculations allow us to calculate the properties of the shock structure, like its width or its asymmetry. However, the shock structure is usually very thin, and the temptation is great to approximate it by an actual discontinuity separating the upstream equilibrium, characterised by ρ_i, v_i, and T_i, from the downstream equilibrium, characterised by ρ_f, v_f, T_f. In that case, if the shock occurs in an ideal gas, the equations of balance of mass, momentum and energy imply the Rankine-Hugoniot conditions[82]

$$\frac{p_f}{p_i} = 1 + \gamma M_i^2 \left(1 - \frac{\rho_i}{\rho_f}\right) \quad \text{and} \quad \frac{p_f}{p_i}\frac{\rho_i}{\rho_f} = \frac{\gamma - 1}{2\gamma}\left(\frac{\rho_i}{\rho_f} + 1\right)\left(\frac{p_f}{p_i} - 1\right),$$

which determines ρ_f and p_f in terms of ρ_i and p_i and of the Mach number M_i before the shock. γ is the ratio of specific heats.

There is a price to be paid for the approximation. Indeed, the Rankine-Hugoniot conditions permit both: compression shocks for supersonic velocities $M_i > 1$ and rarefaction shocks for subsonic velocities $M_i < 1$. In reality, however, subsonic shocks do not occur, nor are subsonic shock *structures* permitted by extended thermodynamics on account of dissipation represented by positive values of thermal conductivity κ and viscosity η. So, since κ and η do not occur in the Rankine-Hugoniot theory, dissipation must be *imposed*, as it were, by the requirement that the entropy grow across the shock. That additional requirement forbids rarefaction shocks.

In engineering applications the thickness of the shock structure is often – or mostly – negligibly small in comparison with the dimensions of an airfoil (say), or a diffuser which is a jet with an increasing cross-section. The engineers are well-satisfied with the Rankine-Hugoniot theory. It is only in *rarefied* gases that this approximation becomes unsatisfactory, because the thickness of the shock structure becomes comparable with the dimensions of the aerodynamic components. In such cases extended thermodynamics or molecular dynamics is called upon to make the correct predictions.

9.7 Symmetry of production coefficients

We recall the form $(9.9)_2$ of the production terms appropriate to extended thermodynamics of moments. Since the Lagrange multipliers Λ_β ($\beta = 4, 5 \ldots n - 1$) vanish in equilibrium, we may easily find the *linear* relation between Π_α and Λ_β ($\alpha, \beta = 4, 5 \ldots n - 1$). It reads

$$\Pi_\alpha =$$

$$\left[\underbrace{\sum_{\beta=5}^{n-1} \frac{1}{4}\mu^2 \frac{1}{k} \int \left(c_\alpha + c_\alpha^1 - c_\alpha' - c_\alpha^{1'}\right)\left(c_\beta + c_\beta^1 - c_\beta' - c_\beta^{1'}\right) f_E(c) f_E(c_1) rV \sin\Theta \, d\Theta \, d\varepsilon \, dc \, dc_1}_{L_{\alpha\beta}}\right] \Lambda_\beta.$$

$$(9.16)$$

---

[82] Cf. the Chapman-Jouguet conditions of Section 6.5.

Obviously the matrix of coefficients L_{ab} is symmetric. This result was discovered by Wen-An Yong in a paper in which he advertised hyperbolic systems with entropy inequalities [Yong 2007][83]. To give Yong proper credit it must be said, that *he* did not restrict the attention to linear relations for Π_α. The analysis for the general case is too intricate to be presented here; in fact it is quite ingenious. Wen-An Yong considers his result as *a non-linearisation of the celebrated Onsager reciprocity relations on modern thermodynamics.* And maybe he is right, maybe the Onsager relations should be formulated for productions rather than rate laws or fluxes.

We recall from our earlier discussion of Onsager relations that there is some uncertainty as to the proper choice of forces and fluxes that are to be related by a symmetric matrix. Indeed, if the relations hold for one such choice, they will generally not hold for another one. Yong's analysis suggests that the *proper* choice is productions and Lagrange multipliers. This indicates yet another attractive trait of the privileged field, the field of Lagrange multipliers.

9.8 Extended thermodynamics consistent in order of magnitude. Boundary conditions for large-rank moments

In the consideration of light scattering and shock structures the increase of the tensorial rank of moments has been an efficient manner to proceed from theories of dense gases to those of rarefied ones. Plausible as this might be, it seems desirable to have a less arbitrary, and more physical criterion for choosing the proper *extension* for the extant degree of rarefaction. And indeed, all moments can be characterised as being of *zero*th, first, second, third, ... order of magnitude in terms of powers of the mean free path or the mean time between collisions of the atoms[84].

Such a classification of moments is already indicated in Grad's work [Grad 1949], and it is systematically exploited in a theory dubbed Consistent-Order Extended Thermodynamics [Müller 2002]. The classification scheme is too complex to be described here in detail. However let it be said

- that *zero*th and first order theories in the new scheme correspond to the Euler fluid and the 13-moment approximation, respectively;
- that *grosso modo* increasing the orders of magnitude is tantamount to increasing the tensorial rank of moments and;
- that closure is an automatic consequence of the assignment of the necessary order.

The consistent scheme has been summarised and further developed by Reitebuch [Reitebuch 2005]. It turns out that the lowest order in the consistent scheme that leads to a *linear* modification of Fourier's law is order 4(!). Thus moments of up to a tensorial rank of 7 need to be considered. The governing equations are linear and so they may easily be solved. The problem is the formulation of boundary and initial conditions, e.g. for an internal moment of the type ρ_{iijjkl}. In the stationary case, the task of prescribing and maintaining the boundary conditions remains.

A possible solution to that problem has been indicated by Reitebuch for the case of stationary one-dimensional heat conduction in a gas at rest between two plates. Since obviously ρ_{iijjkl} cannot be assigned on the boundary by the experimenter, the gas must choose a suitable value by itself, so to speak. One may conceive the idea, – see [Barbera 2004] –, that the uncontrollable boundary values fluctuate along with the

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[83] The title of the paper is obviously styled after Godunov's important paper which first called attention to symmetric hyperbolic systems, see Section 8.

[84] In a non-dimensionalized theory the moments are said to be of different powers in *Knudsen number*. That positive number measures the rarefaction of a gas: the smaller it is the denser is the gas.
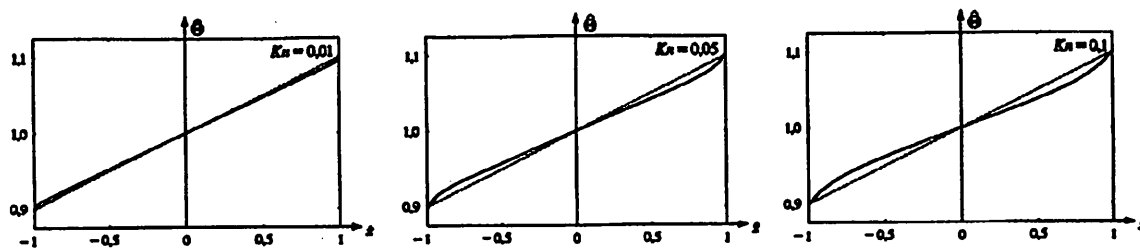
Fig. 23. Temperature field in a rarefied gas between parallel plates for increasing Knudsen numbers. (The straight dashed line represents Fourier's solution).

rapid thermal motion, and that the gas responds to the mean values of the fluctuating moments. According to Boltzmann's definition (2.7), (2.8) of entropy, the probability of the fluctuating boundary values may then be determined from the entropy. On this basis one can calculate the temperature field between the plates and it turns out that there are exponential boundary layers in temperature near the plates, while otherwise the field of temperature is pretty much linear as in Fourier's theory. See Figure 23.

Similar boundary layer solutions have been calculated by the numerical solution of the Boltzmann equation, see [Ohwada 1996], and this lends some support to the *fluctuation theory* for boundary values. Of course, people like Ohwada, working with the Boltzmann equation have their own problems with boundary values for the distribution function. If anything, these problems are more severe than those of consistent-order extended thermodynamics.

10 Outlook

As this report on irreversible thermodynamics has been developed in Sections 1 through 9 it has concentrated more and more on ideal gases, even monatomic ideal gases. Such concentration on an extremely special case was forced upon us, because extrapolation of Eckart's theory into the non-linear regime requires a guideline and the kinetic theory of gases provides such a guideline. Thus, we were able to formulate explicit non-linear corrections of the classical laws of Navier-Stokes and Fourier in rarefied gases and to incorporate those in extended thermodynamics.

It is our confident hope that eventually all of irreversible thermodynamics can be formulated such as to conform to the elegant formal structure presented in Section 8.4 with symmetric hyperbolic field equations in the appropriate variables. Essentially this will require the identification of the densities u_α ($\alpha = 0, 1, \ldots n$) and the formulation of constitutive equations for fluxes and productions of the form (8.17) – a formidable task. We cannot hope, perhaps, that in all cases the densities are moments of some distribution function which is governed by a Boltzmann-type transport equation.

And yet, there are several cases where we *do have* kinetic theories and a distribution function for the constituent particles. Common to all of them is the observation that the particles have large mean free paths and large mean times of free flight, so that transport equations of Boltzmann-type can be formulated, albeit with different production terms, usually simpler ones than Boltzmann's non-linear Stosszahlansatz. The corresponding moment equations offer a heuristic guideline for the formulation of irreversible thermodynamics. Theories of that type describe

- relativistic thermodynamics of very hot gases [Liu 1986];
- electrons in a metal [Sommerfeld 1956];
- photons in a scattering medium [Struchtrup 1996; 1997; 1998a];
- phonons in crystalline solids [Struchtrup 1991; 1998b];
- phonons in semiconductors [Anile 1996].

The basic tenets and results of these theories of somewhat esoteric particles are reviewed in the book by Müller and Ruggeri [Müller 1998].

Non-Newtonian fluids, so-called rheological fluids, deserve a special mention in this context and some comment, because we recall from Section 5 that a naïve attempt to describe non-Newtonian behaviour failed in rational thermodynamics and it helped to bring down claims that the theory could deal with such visco-elastic fluids. Therefore there is the pressing need for new ideas in that field, and here is one for future development:

It so happens that for rheological fluids a well-developed kinetic theory is available. Often such fluids are solutions of a Newtonian solvent and a polymeric solute. On account of the large size of the polymer molecules the solute suffers a non-local interaction with the solvent by virtue of Stokes's law of friction, see (1.4), because the ends of the molecules feel solvent velocities at different points. In the rheological literature that mechanism has served as the basis for a kinetic theory to which Bird is one of the most prominent contributors [Bird 1971; Curtiss 1976]. See also the less comprehensive attempt by Müller to derive the governing equations for stress and heat flux in a dumbbell solution [Müller 1979].

Within the kinetic theory of dumbbell solutions it is possible to develop a moment theory very similar in spirit to the moment theory in the kinetic theory of gases, or the moment theory of phonons. Closure may be achieved by a Grad-type expansion for the distribution of dumbbells. Such a systematic approach toward extended thermodynamics of rheological fluids has not yet been followed through, although some tentative first steps in the right direction were made by Giesekus as early as 1956 [Giesekus 1956].

It is natural, perhaps, that the non-Newtonian contributions to the stress have received more attention than the non-Fourierian contributions to the heat flux. Both theory and experiment concentrate on the stress. Thus, in a shear flow between parallel plates of distance h and relative velocity V the shear stress τ is no longer proportional to V/h with the viscosity η as a constant of proportionality. It turns out that a rheological fluid exhibits an *apparent viscosity*

$$\eta_{app} = \frac{\tau}{V/h}, \tag{10.1}$$

which itself depends on V/h so that a viscometer provides the same viscosity when V and h are changed by the same factor. A more prominent phenomenon, perhaps, is due to the fact that the stress in a rheological fluid has unequal normal components. These components make it impossible for the fluid to move parallel to the walls in a flow through a pipe with non-circular cross section. Inside the pipe there are *secondary flows* with velocity components orthogonal to the walls. That phenomenon was predicted by Ericksen [Ericksen 1956], and experimentally confirmed by Giesekus.

All this is not to say that it is only rarefaction or large mean free paths of constituent particles that requires a reformulation – an extension, as it were – of conventional thermodynamic theories like TIP. It can happen that a new phenomenon requires a new thermodynamic field and therefore a new field equation, but otherwise fits well into the conventional scheme. A case in point is liquid crystals.

The most evident observation in liquid crystals is that they are opaque at low temperature and transparent at high temperature. In the opaque phase the liquids exhibit flow properties which are incompatible with the properties of Navier-Stokes fluids. Such properties have suggested a microscopic anisotropy, to wit, a preferred direction characterising a fluid particle along with – and in addition to – its density, velocity and temperature.

There are two ways to characterise the anisotropy: (1) by a director field d_i with $d_i d_i = $ const. and (2) by an alignment tensor $M_{ij} = s n_i n_j + \frac{1}{3}(1 - s)\delta_{ij}$ with $n_i n_i = 1$

and with a temperature-dependent *degree of orientation* s, ($0 \leq s \leq 1$). Ericksen, following the early research work by Oseen, 1921 and Frank, 1958, adopted the director approach, while de Gennes preferred the alignment tensor. The latter has the advantage that it can incorporate the transition to isotropy at high temperature, if s is properly adjusted as a function of temperature [Ericksen 1976; deGennes 1974]. See also the instructive book by Virga which includes references to the pertinent literature and the characterisation of different types of liquid crystals: nematic, cholesteric, and smectic ones [Virga 1994].

Ericksen's theory was developed into a proper branch of irreversible thermodynamics by Leslie [Leslie 1968]. In some sense the Ericksen-Leslie theory of nematic liquid crystals may be interpreted as a branch of extended thermodynamics, because it extends the list of variables of ordinary thermodynamics, – viz. ρ, v_i, T – by the director d_i. It also extends the classical conservation laws for mass, momentum, and energy by the conservation law of angular momentum, consisting of moment of momentum and spin. Consequently the theory allows the stress to be non-symmetric; recall that all through this report we have – tacitly – assumed that the stress tensor is symmetric. That assumption is well justified for all non-polar fluids, but not for bodies with an intrinsic spin.

The Ericksen-Leslie theory provides a full set of field equations for the variables ρ, v_i, T and $d_{i.}$. The well-known dissipative *mechanisms* of friction and heat conduction are present in the theory, and there is one more mechanism due to the rate of reorientation of the directors. As always in extended thermodynamics boundary values are a problem, but it turns out – fortunately (!) – that walls can be prepared so that either d_i is orthogonal to a wall, or parallel in given direction. Leslie presents the solution of a problem that is particularly well-suited to illustrate the difference between a liquid crystal and a rheological fluid: the isothermal shear flow, between two plates, the paradigm of non-Newtonian flow properties. Leslie assumes no-slip conditions for the velocity and forces the directors at the plates to be aligned in the flow direction. Away from the boundaries he calculates a non-parallel orientation field of the directors. Also, the velocity field is not linear between the plates as it would be in a Newtonian fluid. It turned out that the liquid crystal exhibits an apparent viscosity of the type (10.1), but with η a function of the product Vh rather than the quotient V/h. Thus the same viscosity is measured in a viscometer for a situation with an increase V and an h decreased by the same factor. One often expresses this by saying that rheological fluids *scale differently* from liquid crystals. Anyway, the phenomenon shows that the flow field is affected by the director and that the director affects the flow.

Of course, we all know that the technological significance of liquid crystals is due to their interaction with electro-magnetic fields and not due to the interaction with the flow field. That aspect is not considered here. But let it be said, that the Ericksen-Leslie theory can be used to describe the electro-magnetic effects as well.

Finally a remark on solids. The irreversible thermodynamics of solids is not well developed. Solids have no viscosity to speak of, at least none due to momentum exchange as in fluids and gases. Heat conduction is present, of course, and it is satisfactorily described by Fourier's law under all ordinary circumstances.

However, the most important phenomena in thermodynamics of solids are phase transitions: solid-solid phase transitions between different lattice structures, or between a lattice phase and an amorphous phase. This is an equilibrium phenomenon, except that as a rule in solids such a transition is accompanied by hysteresis. A hysteretic transition proceeds slowly – quasistatically – and yet it is irreversible and far from equilibrium. The nature of the meta-stable states in a hysteretic transition is not fully understood – at least not fully described – and therefore solid-solid-phase

transitions have not been incorporated satisfactorily into irreversible thermodynamics. See, however, [Ericksen 1991; Fu 1993].

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