IRREVERSIBLE PROCESSES IN QUASI-EQUILIBRIUM

Stephen F. Gull and Anthony J.M. Garrett

Dedicated to the memory of Robert Simpson Silver (1913–1997)

- We develop the ideas of Bob Silver, who in 1971 published a textbook *An Introduction to Thermodynamics*, subtitled *with new derivations based on real irreversible processes*.
- Silver's point was that many irreversible thermodynamic processes are in a state of quasi-equilibrium.
- At the 1994 MaxEnt conference Silver emphasised that the Seebeck, Peltier and Thomson thermoelectric effects are all easily understood in terms of a passive flow of electrons *around* the circuit whilst heat flows *through* the circuit.
- He stressed the similarity between the thermocouple and a gravity-driven hot water system, where there is a passive flow of water *around* the circuit whilst heat flows *through* the circuit.
- In this talk we illustrate Bob's ideas applied to: (a) a gravity-driven hot water system; (b) thermoelectric effects; (c) the internal structure of shock fronts; (d) hydraulic jumps.

SILVER'S SECOND LAW OF THERMODYNAMICS AND THERMOELECTRICITY

- The first law of thermodynamics: $\mathrm{d}U = đQ + đW = T\mathrm{d}S - P\mathrm{d}V$.
- For a cyclic process: $\oint \mathrm{d}U = 0 \Rightarrow \xi \equiv \oint T\mathrm{d}S = \oint P\mathrm{d}V = -\oint S\mathrm{d}T = -\oint V\mathrm{d}P$.
- The "energy area" ξ represents the potential to do work or to drive heat through the system.
- The second law of thermodynamics is $T\mathrm{d}S \geq đQ$, with equality if the process is reversible.
- By considering the work done by friction $đW_{\mathrm{f}}$, Silver converts this law to an **equality**:

$$T\mathrm{d}S = đQ + đW_{\mathrm{f}}.$$

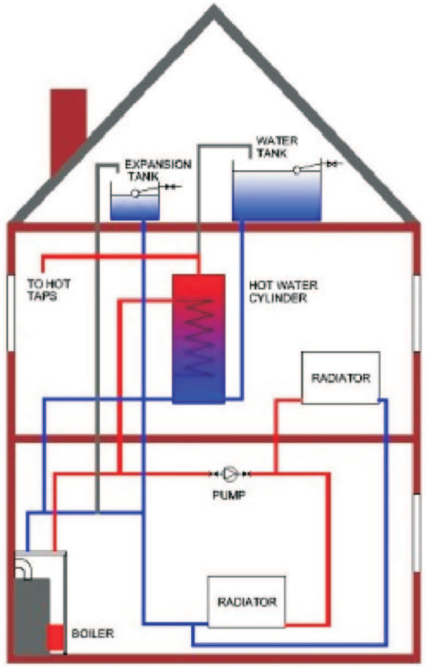
- As an example, Silver treats the phenomenon of thermoelectricity: the Seebeck,Peltier and Thomson effects.
- He notes that the electromotive force (EMF) around a thermocouple circuit can be written $\mathcal{E} = \oint S\mathrm{d}T$ where S are the Seebeck coefficients of the materials comprising the circuit.
- The similarity to the relation $\xi = -\oint S\mathrm{d}T$ above is obvious, although the EMF is in Volts, rather than energy units. Nevertheless, it strongly suggests that the Seebeck coefficient of a material represents the entropy per unit charge S_{q} of a thermoelectric material.

Gravity-Driven Hot Water System

- Silver emphasised the similarity between quasi-equilibrium in an gravity-driven hot water system and the thermocouple.

- I have tried to remember the operating parameters of the 1954 kitchen stove in St. Albans that provided the water for my weekly bath in a galvanised tub on the kitchen floor.

- We make a model of the system with a lagged hot vertical pipe of height h, containing water at density ρ_2, and a lagged cold pipe of length h with water of density ρ_1.



GRAVITY HOT WATER SYSTEM

- There is heat input to the system $\dot{Q}$ at the boiler and an output $\dot{Q}$ at the hot water tank.

- Resistance to the flow is provided by laminar, viscous flow in the pipes (we ignore the resistance in the boiler and tank). The volume flow rate is given by the famous Hagen-Poiseuille formula (1840): $\dot{V} = \frac{\pi a^4}{8\eta} \left| \frac{\mathrm{d}P}{\mathrm{d}z} \right|$ where a is the radius of the pipe (diameter 22 mm), $\eta = 8.9 \times 10^{-4}$ Pa s is the viscosity of water and $\mathrm{d}P/\mathrm{d}z$ is the pressure gradient driving the flow.

- If the pressure at the boiler is P_B, then the pressure at the tank P_T can be calculated: $P_\mathrm{T} = P_\mathrm{B} - \rho_1 gh + h|\mathrm{d}P/\mathrm{d}z| = P_\mathrm{B} - \rho_2 gh - h|\mathrm{d}P/\mathrm{d}z| \Rightarrow |\mathrm{d}P/\mathrm{d}z| = \frac{1}{2}g(\rho_1 - \rho_2)$ so that the pressure gradient is independent of the height h.

- Suppose that the difference in temperature between the input and output of the boiler is $\Delta T = 20\ \mathrm{K}$. The thermal expansion coefficient of water is 6.9×10^{-5} K^{-1}, so that the volume flow rate 43 ml s^{-1} and the average flow velocity is 11 cm s^{-1}.

- The literature on pipe flows confirms that the flow is indeed (almost) laminar for these parameters. Evaluating the heating rate we get a respectable 3.7 kW.

- The P–V diagram for the hot water system has $\xi = (P_\mathrm{B} - P_\mathrm{T})\Delta V\,(\Delta V \equiv V_2 - V_1)$.

- The rate of frictional work $\dot{W}_\mathrm{f} = \dot{V}\Delta P$. The time taken to complete one cycle is $V/\dot{V}$, so the total $W_\mathrm{f} = V\Delta P$.

- In quasi-equilibrium $Q = 0$ (no net heat input). Using $\Delta V/(V/2) \approx -\Delta\rho/(\rho)$ we find $W_\mathrm{f} = \xi$, as predicted by Silver.

The Thomson Effect

- Consider a current-carrying wire with a thermal gradient along its length which is in quasi-equilibrium. The thermodynamic state of the wire is not varying with time, but the state variables vary along its length, and irreversible dissipation is occurring due to the resistance.
- If the charge/mass ratio of the current carriers is q/m, define $S_{\mathrm{m}} = S_{\mathrm{q}} q/m$ to be the entropy *per unit mass* of the material in the wire.
- If the mass flow rate is $\dot{M}$, we find $\dot{M} T \mathrm{d} S_{\mathrm{m}} = \dot{M} đ Q + \dot{M} đ W_{\mathrm{f}} \equiv \dot{Q} \mathrm{d}x + \dot{W}_{\mathrm{f}} \mathrm{d}x$ where $\dot{Q}$ and $\dot{W}_{\mathrm{f}}$ are the total heat input and frictional work per unit length of the wire.
- The total heat input $\dot{Q}$ must include a contribution from the ambient medium $\dot{Q}_{\mathrm{am}}$ and also the effects of heat conduction $\frac{\mathrm{d}}{\mathrm{d}x}\left(\alpha \frac{\mathrm{d}T}{\mathrm{d}x}\right)$: $\quad \dot{Q} = \dot{Q}_{\mathrm{am}} + \frac{\mathrm{d}}{\mathrm{d}x}\left(\alpha \frac{\mathrm{d}T}{\mathrm{d}x}\right)$. where α is the thermal conductivity. The frictional work done is $I^2 r$, where I is the current and r is the resistance per unit length. We therefore have $\dot{M} T \mathrm{d} S_{\mathrm{m}} = \dot{Q}_{\mathrm{am}} \mathrm{d}x + \mathrm{d}\left(\alpha \frac{\mathrm{d}T}{\mathrm{d}x}\right) + I^2 r \mathrm{d}x$
- By definition, the Thomson effect is the reversible thermal energy transmission from the surroundings after allowance for resistive dissipation and conduction effects.

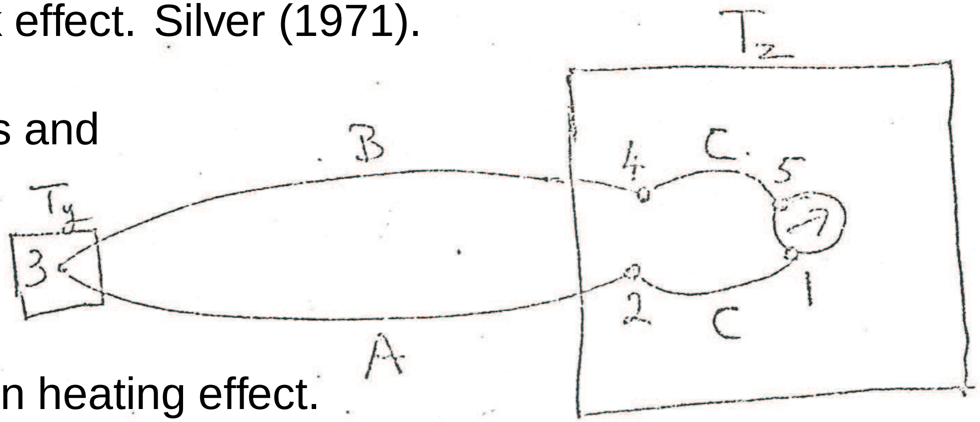
- Denoting the Thomson effect heating per unit length by $\dot{Q}_\theta$, we have therefore $\dot{Q}_\theta \mathrm{d}x = \dot{Q}_{am}\mathrm{d}x + \mathrm{d}\left(\alpha\frac{\mathrm{d}T}{\mathrm{d}x}\right) + I^2 r \mathrm{d}x$ We therefore see that the Thomson effect reflects the change in the entropy across the element; which in turn is due to variation of the entropy $S_\mathrm{m}(T)$ with temperature. As usually defined for a current flowing in a temperature gradient, we have $\dot{Q}_\theta \mathrm{d}x = \kappa I \mathrm{d}T$ where κ is the Thomson coefficient. Since $\dot{M} = Im/q$ we therefore have $\kappa = \dfrac{m}{q} T \left(\alpha \dfrac{\mathrm{d}S_\mathrm{m}}{\mathrm{d}T}\right)$
- This is consistent with the usual definition of the Thomson coefficient if the Seebeck coefficient S is $S = S_\mathrm{q} = S_\mathrm{m} m/q$, the entropy per unit charge.

The Peltier Effect

- The Peltier effect is the generation of heat at the junction of two materials with different Seebeck coefficients, carrying current I. Here we suppose that the entropy *per unit mass* of the materials (a, b) is $S_{\mathrm{m}(a,b)}$. We find $\dot{M}T(S_{\mathrm{ma}} - S_{\mathrm{mb}}) = \dot{Q}^{\mathrm{j}} + \dot{W}_{\mathrm{f}}^{\mathrm{j}} = \dot{Q}^{\mathrm{j}} + I^2 R^{\mathrm{j}}$ where R^{j} is the resistance of the junction.
- Again, $\dot{Q}^j$ has contributions from thermal energy transmitted from the ambient surroundings and thermal conduction effects in the wires at the junction.
- Therefore we have $\dot{Q}^{\mathrm{j}} = \dot{Q}^{\mathrm{j}}_{\mathrm{am}} - \alpha_a \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^{\mathrm{j}}_{\mathrm{a}} + \alpha_b \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^{\mathrm{j}}_{\mathrm{b}}$
- The conventional definitions of the Peltier coefficient $\pi_{a,b}$ and the Peltier heat $\pi_{a,b}I$ is the reversible energy transmission from the ambient surroundings after allowance has been made for resistive dissipation and conduction effects. Hence, $\pi_{(a,b)}I = \dot{Q}^{\mathrm{j}}_{\mathrm{am}} - \alpha_a \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^{\mathrm{j}}_{\mathrm{a}} + \alpha_b \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^{\mathrm{j}}_{\mathrm{b}} + I^2 R^{\mathrm{j}}$
- Using $\dot{M} = Im/q$, the Peltier coefficient is therefore related to the entropy as $\pi_{(a,b)} = \frac{m}{q} T(S_{\mathrm{ma}} - S_{\mathrm{mb}})$ which is identical to Thomson's second thermoelectric relation if the Seebeck coefficient of a material represents the entropy per unit charge.

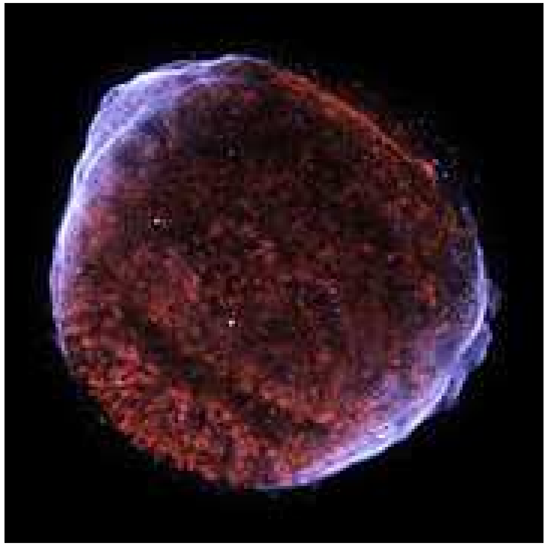
THE SEEBECK EFFECT

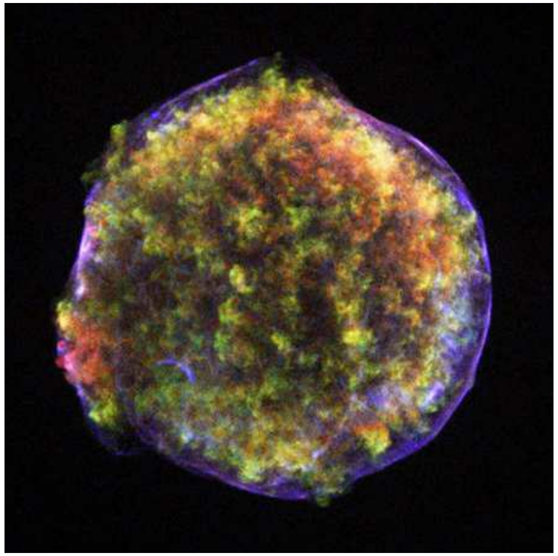
- Thermocouple circuit illustrating the Seebeck effect. Silver (1971).



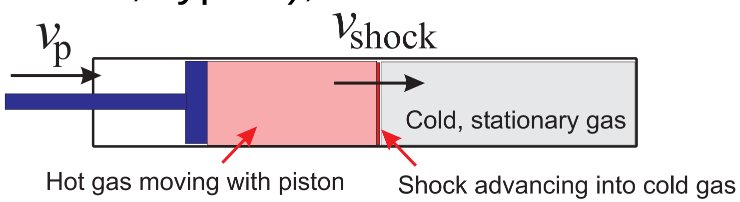
- A, B and C denote wires of different materials and T_y and T_z are two different temperatures.
- At junctions 1 and 5 there are no Peltier effects, and between 1-2 and 4-5 no Thomson heating effect.
- There are three Peltier effects, at junctions 2, 3 and 4, and two Thomson effects, in the wires A and B.
- We shall not go into further details in this talk but, by following the Peltier and Thomson effects derived above around the thermocouple circuit, we can finally prove that the Seebeck coefficient $S = S_{\mathrm{q}} = S_{\mathrm{m}} \frac{m}{q}$ is the entropy per unit charge.
- This direct derivation, due to Silver but essentially that of Thomson (1850), is often quoted only to be dismissed and replaced by one based on the Onsager relations. But it is correct.

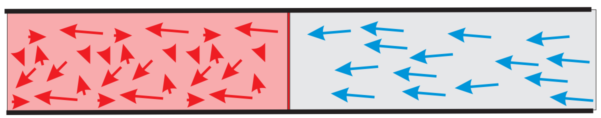
Shocks in Supernova Remnants





- SNR shock fronts, visualised in X-rays. (a) SN1006, the brightest historical supernova (Type Ia). (b) SN1572, famously described by Tycho Brahe (Type Ia). (c) Kepler's SNR (AD1604, Type II), SFG's first radio observational project (1974).





- Supersonic flows are characterised by shock fronts, with a sudden discontinuity of density, pressure and velocity, accompanied by dissipation leading to an increase of entropy.

The Internal Structure of Shock Fronts

- The Rankine-Hugoniot conditions for an adiabatic fluid express the conservation of mass, momentum and energy flux:

$$\begin{aligned} \rho_1 v_1 &= \rho_2 v_2 \\ P_1 + \rho_1 v_1^2 &= P_2 + \rho_2 v_2^2 \\ (u_1 + P_1) v_1 + \tfrac{1}{2}\rho_1 v_1^3 &= (u_2 + P_2) v_2 + \tfrac{1}{2}\rho_2 v_2^3 \end{aligned}$$

  where, for an adiabatic fluid with ratio of specific heats γ, the internal energy per unit volume is $u = P/(\gamma - 1)$. The quantities $\{\rho_1, v_1, P_1\}$ conventionally refer to the upstream values.
- This has the solution $\dfrac{\rho_2}{\rho_1} = \dfrac{v_1}{v_2} = \dfrac{\gamma+1}{\gamma - 1 + 2/M_1^2}$; $P_2 = P_1 + \dfrac{2\rho_1 v_1^2}{\gamma+1}\left(1 - \dfrac{1}{M_1^2}\right)$

  where $M_1^2 = v_1^2 \rho_1/(\gamma P_1)$ is the square of the upstream Mach number.
- In reality, the shock will have a finite thickness, determined by viscosity or non-linear processes – what can we say about the internal structure?
- The fluid entering the shock starts with a velocity v_1 and is again in equilibrium when the velocity reaches v_2.
- As the fluid decelerates, the velocity must, at some stage, pass through all velocities $v_2 < v < v_1$. There must be some additional stress $-\tau$ (an additional pressure).

- The Eulerian fluid equations are:

$$\begin{aligned}\partial_t \rho + \boldsymbol{\nabla}\cdot(\rho \boldsymbol{v}) &= 0 \\ \rho \partial_t \boldsymbol{v} + \rho \boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v} &= -\boldsymbol{\nabla}(P+\tau) \\ \partial_t u + \boldsymbol{v}\cdot\boldsymbol{\nabla} u &= -(u+P+\tau)\boldsymbol{\nabla}\cdot\boldsymbol{v}\end{aligned}$$

- The flow is stationary and one-dimensional, so this simplifies to ($'$ denotes the spatial derivative): $v\rho' + \rho v' = 0$; $\rho v v' = -(P' + \tau')$; $v u' = -(u + P + \tau) v'$.

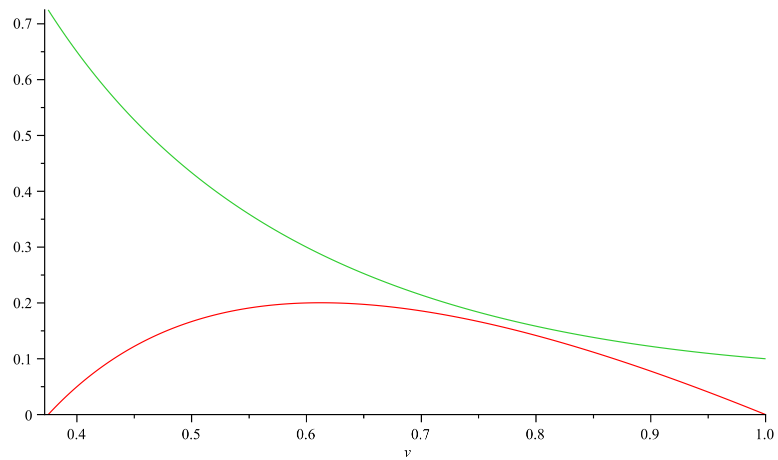
- These equations are easily integrated. In terms of the upstream quantities we have $\rho v = \rho_1 v_1$; $P + \rho_1 v_1 v + \tau = P_1 + \rho_1 v_1^2$.

- Substituting for P in the remaining equation we find an expression for the stress τ:

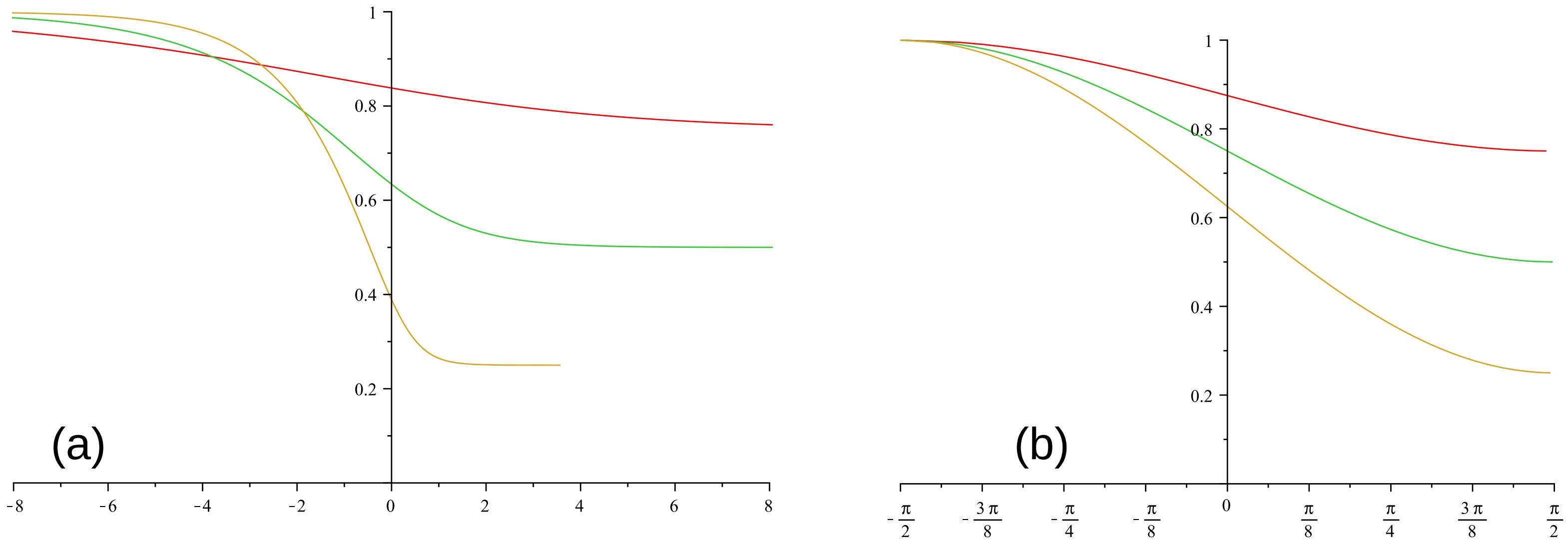
$$\tau(v) v = \tfrac{1}{2}(\gamma+1)\rho_1 v_1 (v_1 - v)(v - v_2)$$

- This extra stress (red curve) goes to zero at $v = v_1$ and $v = v_2$, providing the necessary dissipative forces inside the shock.

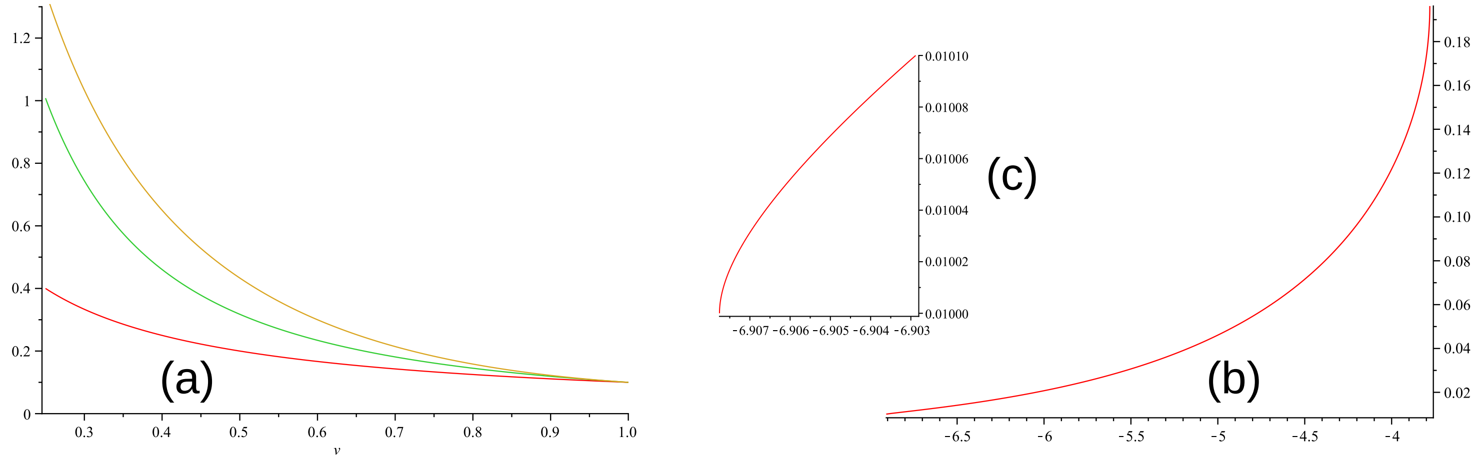
- The green curve is the pressure $P(v)$.



- The structure of the shock is determined by the spatial function $v(x)$. If we knew the shape $v(x)$, we could calculate the stress $\tau(v(x))$.
- Equally, if we know the functional form of $\tau(v,x)$, we can derive $x(v)$ (and hence $v(x)$).
- We have calculated this (a) for a simple viscous model of the stress $\tau(v,x) = \eta \boldsymbol{\nabla} \cdot \boldsymbol{v}$ and (b) a quadratic viscous dissipation $\tau = \eta' \rho (\boldsymbol{\nabla} \cdot \boldsymbol{v})^2$ (often used in numerical codes).



- (a) For case (a) above, stronger shocks are much narrower than weak ones. For case (b) the shocks are finite in extent and all have the same width.



- (a) (From the bottom) Isotherms, adiabats and shock profiles for $\gamma = 5/3$. The plots show P versus v, but that is the same as a P–V diagram for this case ($v \propto 1/\rho$).The pressure in a shock rises more steeply than adiabats or isotherms.

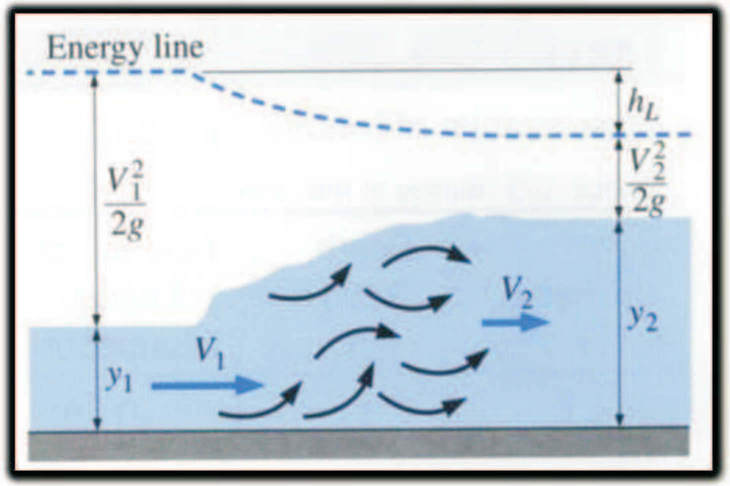
- (b) T–S diagram for a shock. (c) Inset shows behaviour of T–S diagram near $v = v_1$ – the slope becomes infinite, as predicted for $\tau = 0$.

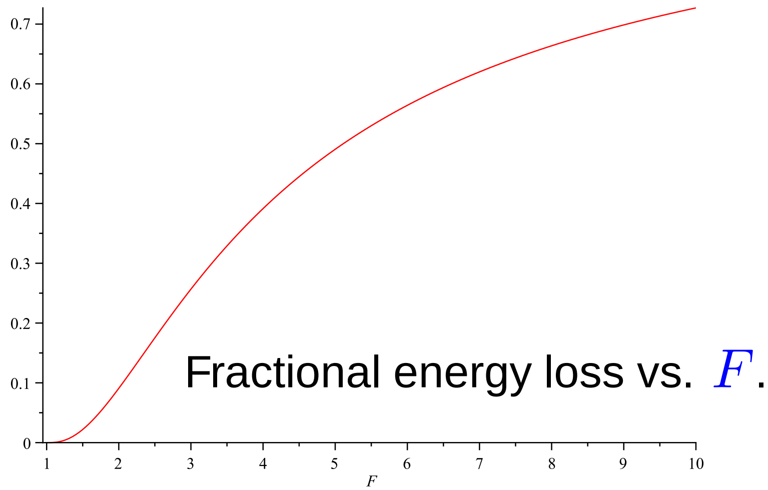
- The pressure and entropy are calculated from using the perfect gas law.

- From the T–S relation we find $\dot{U} = -(p+\tau)\dot{V} = T\dot{S} - P\dot{V}$ so that $T\mathrm{d}S = -\tau\mathrm{d}V = \text{đ}W_\mathrm{f}$.

- No heat enters or leaves the system $(\text{đ}Q = 0)$, so again we have Silver's $T\mathrm{d}S = \text{đ}W_\mathrm{f}$.

Hydraulic Jumps





- For incompressible flow in a uniform 1-D channel of depth y the continuity equation is $vy = \mathrm{constant}$, where v is the velocity.
- Bernoulli's equation (where applicable) says $\frac{P(z)}{\rho g} + \frac{v^2}{2g} + z = H = \mathrm{constant}$ where z is the depth ($0 < z < y$). The constant H is the "head", and is measured in metres.
- Conservation of the momentum flux gives $\rho v_1^2 y_1 + \frac{1}{2}\rho g y_1^2 = \rho v_2^2 y_2 + \frac{1}{2}\rho g y_2^2$.
- The Froude number $F^2 = v_1^2/(gy_1)$, is ratio of the velocity to the wave speed $\sqrt{gy_1}$.
- Solving, we find $\frac{y_2}{y_1} = \frac{\sqrt{1+8F^2}-1}{2}$ which gives jump condition provided $F > 1$.
- The fraction of energy $\rho v^2 y + \frac{1}{2}\rho g y^2$ dissipated can be calculated and is shown above.

CONCLUSIONS

- The Second Law is an **equality** if the work done by friction is taken into account: $T\mathrm{d}S = đQ + đW_{\mathrm{f}}$. This law sheds light on many irreversible processes in quasi-equilibrium.
- The old-fashioned gravity-driven hot water system is analogous to the thermocouple.
- The thermoelectric Seebeck coefficient is the entropy per unit charge of the charge carriers.
- Thomson's second relation $\pi_{a,b} = T(S_a - S_b)$ is proved by a direct argument, and does *not* depend on Onsager's theory.
- Shock fronts provide another example of an irreversible processes in quasi-equilibrium. We can determine many of the internal properties of shocks and even their spatial structure (we would love to see some experimental evidence!).
- Hydraulic jumps are yet another example of an irreversible processes in quasi-equilibrium.
- So is the Joule-Kelvin effect, but we didn't have time to describe it here.