On the roles of energy and entropy in thermodynamics

by

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$$q_i = -\kappa \frac{\partial T}{\partial x_i}$$

J.B. Fourier

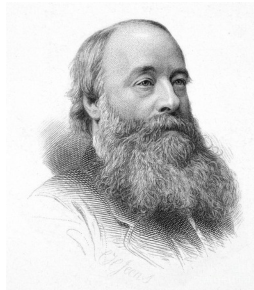
$$t_{ij} = 2\mu \frac{\partial v_{<i}}{\partial x_{j>}} + \nu \frac{\partial v_l}{\partial x_l} \delta_{ij}$$

G. G. Stokes

C.-L. Navier

Derivations did not require the knowledge of the nature of heat, let alone the concepts of energy and entropy

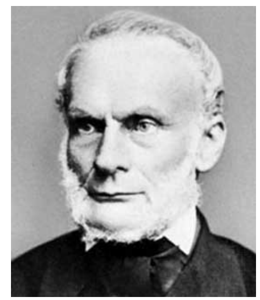

R. J. Mayer


J. P. Joule


H. v. Helmholtz

First Law: $$\frac{dE}{dt} = \dot{Q} + \dot{W}$$


S. Carnot


R. Clausius

Second Law: $$\frac{dS}{dt} \geq \frac{\dot{Q}}{T_0}$$

probabilistic interpretation $$S = k \ln W$$


L. Boltzmann

$$\Longrightarrow \quad A \equiv E - T_0 S \rightarrow \text{Minimum in equilibrium}$$

Minimal energy is conducive to equilibrium and so is maximal entropy. Temperature is control parameter.

Competition between determinism by which energy approaches a minimum

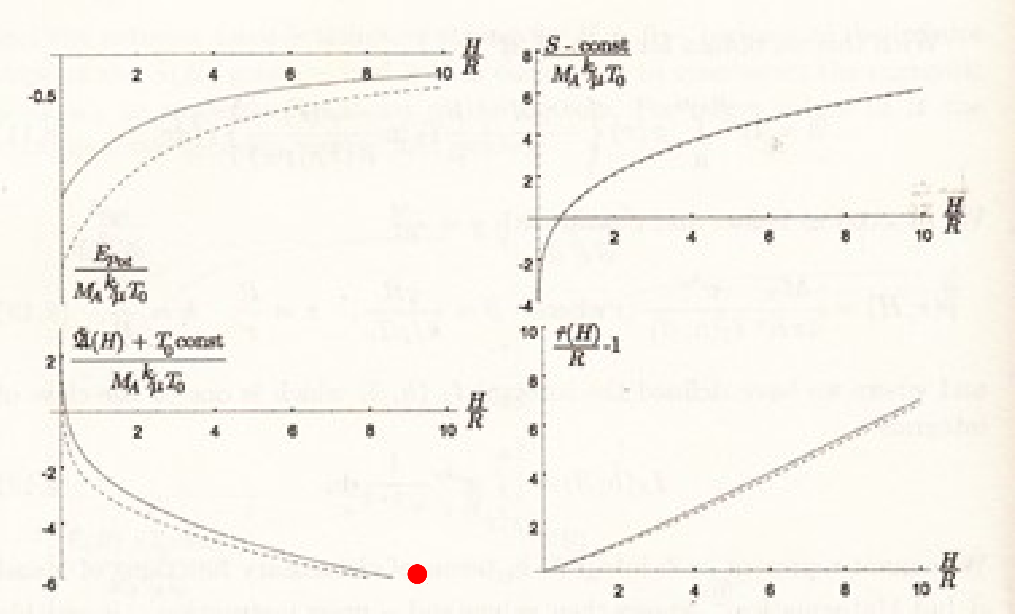
and stochasticity by which entropy approaches a maximum.

Planetary Atmospheres

Energy of atmosphere is minimal when all air molecules lie on the solid surface.

Who wins?

Entropy is maximal when air molecules are evenly distributed throughout space..



Relevant parameter $$\beta = \frac{\gamma \frac{M}{R}}{\frac{k}{\mu} T}$$

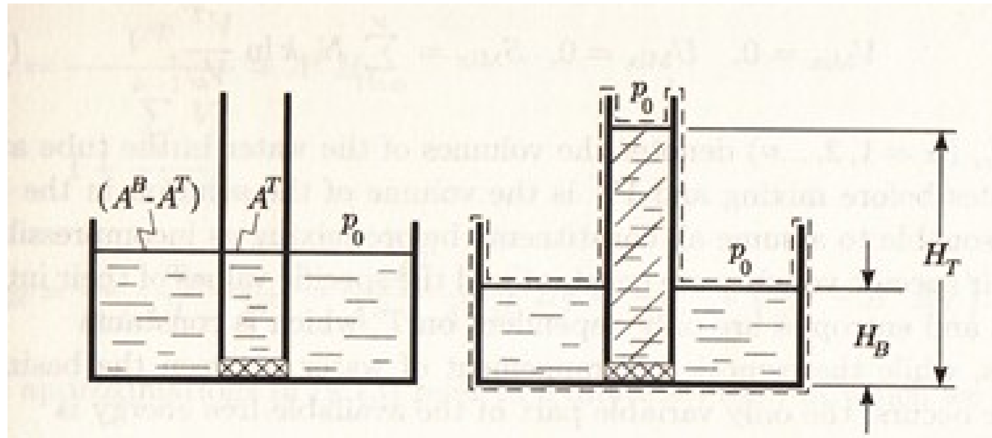
Mercury and Moon have already lost their atmospheres

Jupiter, Saturn and Uranus have kept even light gases

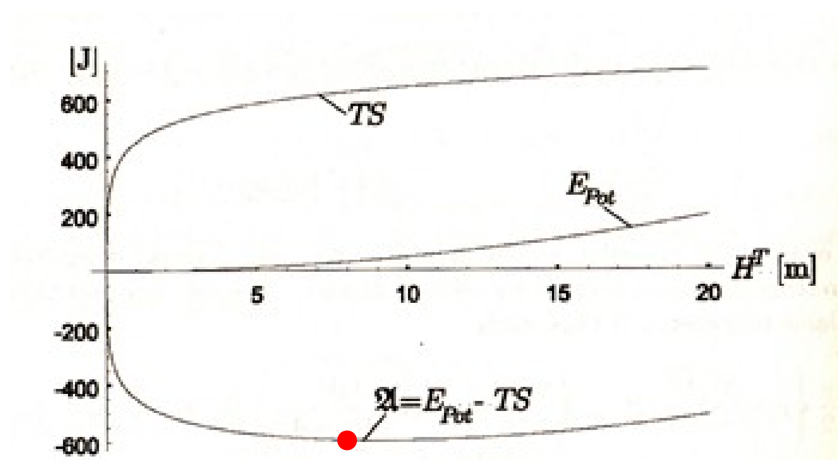
Earth hangs on to oxygen and nitrogen – for he the time being !

Osmosis

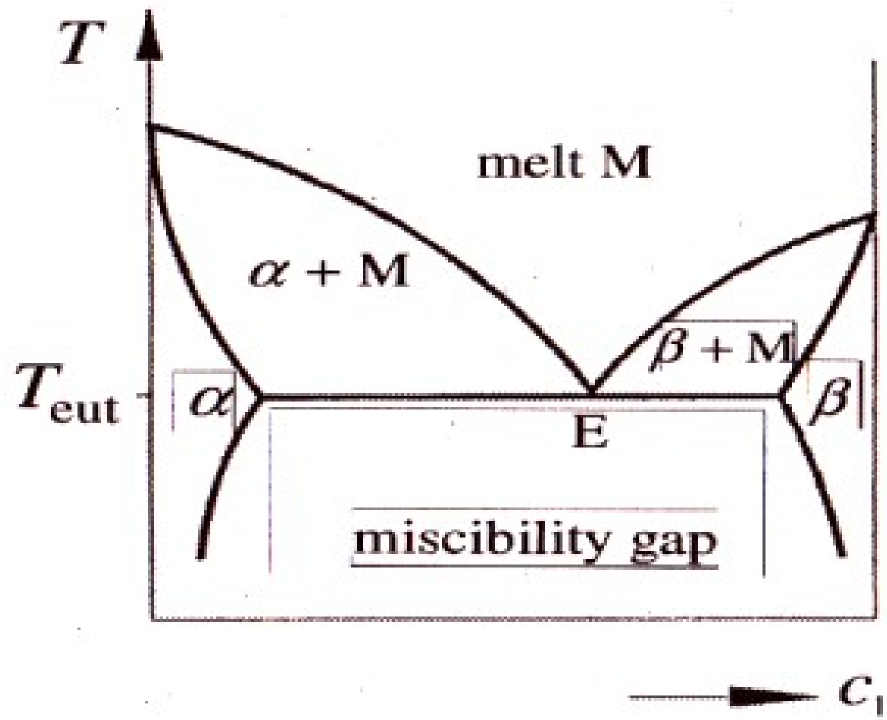
Pfeffer tube



W. Pfeffer



Phase Diagrams (for alloys and solutions)



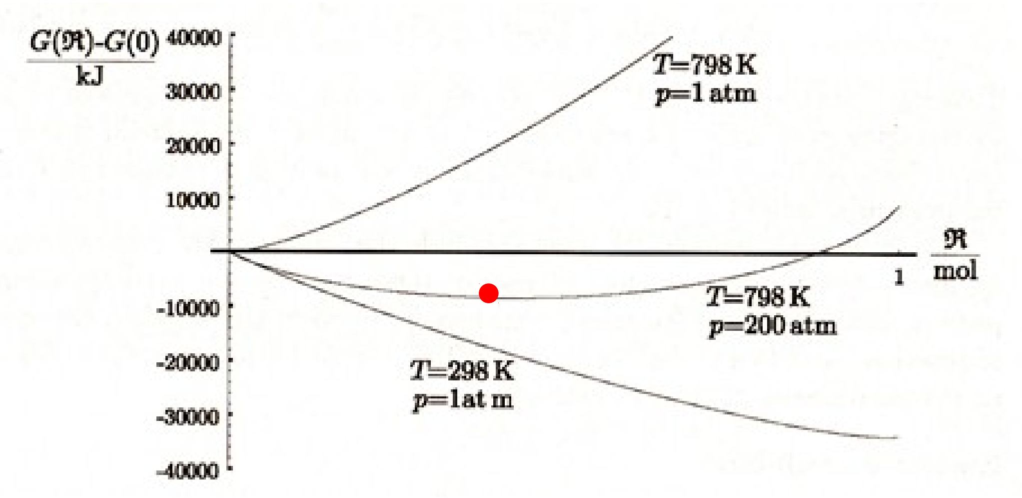
Ammonia Synthesis (Haber-Bosch)

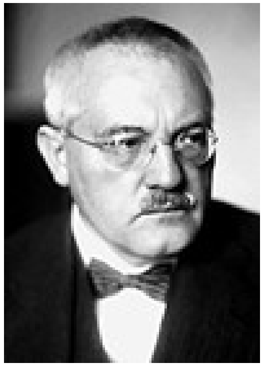
$$3H_2 + N_2 \rightarrow 2NH_3$$

$$\Delta h = -3h^{H_2} - h^{N_2} + 2h^{NH_3} = -92.4\,\frac{kJ}{mol}$$

$$\Delta s = -3s^{H_2} - s^{N_2} + s^{NH_3} = -178.6\,\frac{J}{mol\,K}$$

F. Haber





K. Bosch

Doctrine of Forces and Fluxes (TIP)

Gibbs equation

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

$\Uparrow$	$\Uparrow$	$\Uparrow$
energy balance	mass balance	partial mass balance

Entropy Inequality

$$\rho \frac{ds}{dt} + \frac{\partial}{\partial x_i}\left(\frac{q_i - \sum_{\alpha=1}^{\nu} g_\alpha J_i^\alpha}{T} \right) =$$

$$= -\frac{1}{T}\sum_{a=1}^{n}\left(\sum_{\alpha=1}^{\nu} g_\alpha \gamma_\alpha^a \mu_\alpha \right)\lambda^a + q_i \frac{\partial \frac{1}{T}}{\partial x_i} - J_i^\alpha \frac{\partial \frac{g_\alpha}{T}}{\partial x_i} + \frac{1}{T} t_{<ij>} \frac{\partial v_{<i}}{\partial x_{i>}} + \frac{1}{T}\left(\frac{1}{3} t_{ii} + p \right)\frac{\partial v_l}{\partial x_l} \geq 0$$

Thus follows a semi systematic derivation for the laws of Fourier, Navier-Stokes and Fick by linear relations between forces and fluxes.

Fully satisfactory for liquids and dense gases.
But deficient when rates of change are rapid and gradients are steep as may easily happen in rarefied gases

Extended Thermodynamics

Fields u_α **(α=1,2, ...N)**

Field equation $$\frac{\partial u_\alpha}{\partial t}+\frac{\partial F_\alpha^i(u_\beta)}{\partial x_i}=\Pi(u_\beta)$$ **Solutions: Thermodynamic processes**

Entropy Principle $$\frac{\partial h}{\partial t}+\frac{\partial h^i(u_\beta)}{\partial x_i}=\Sigma(u_\beta)\geq 0$$ **for all thermodynamic processes and $h(u_\alpha)$ concave**

$$\Rightarrow \quad \frac{\partial h}{\partial t}+\frac{\partial h^i(u_\beta)}{\partial x_i}-\Lambda_\alpha\left(\frac{\partial u_\alpha}{\partial t}+\frac{\partial F_\alpha^i}{\partial x_i}-\Pi\right)\geq 0$$ **for all fields** $u_\alpha(x_i,t)$

Change of fields $u_\alpha \Leftrightarrow \Lambda_\alpha$ **Field equations** $$\frac{\partial^2 h'}{\partial\Lambda_\alpha\partial\Lambda_\beta}\frac{\partial\Lambda_\alpha}{\partial t}+\frac{\partial^2 h'^i}{\partial\Lambda_\alpha\partial\Lambda_\beta}\frac{\partial\Lambda_\alpha}{\partial x_i}=\Pi_\alpha$$

$\Uparrow$
symmetric hyperbolic !!

Conclusion: Entropy Principle guarantees that the field equations are symmetric hyperbolic.
Initial value problems well-posed:
- **existence and uniqueness of solutions**
- **continuous dependence of solutions on initial data**
- **finite characteristic speeds**

Extended Thermodynamics of 21 Moments (and partial systems)

Euler

$$\frac{\partial \varrho}{\partial t} + \bar\varrho \frac{\partial v_k}{\partial x_k} = 0$$

$$\frac{\partial v_i}{\partial t} + \frac{\frac{k}{\mu}\bar T}{\bar\varrho}\frac{\partial \varrho}{\partial x_i} + \frac{\partial \frac{k}{\mu}T}{\partial x_i} - \frac{1}{\bar\varrho}\frac{\partial t_{<ij>}}{\partial x_j} = 0$$

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

$$\frac{\partial t_{<ij>}}{\partial t} - \frac{4}{5}\frac{\partial q_{<i}}{\partial x_{j>}} - \frac{\partial \varrho_{<ijk>}}{\partial x_k} - 2\bar\varrho\frac{k}{\mu}\bar T\frac{\partial v_{<i}}{\partial x_{j>}} = -\frac{2}{3}\frac{1}{\tau}t_{<ij>}$$

$$\frac{\partial q_i}{\partial t} - \frac{k}{\mu}\bar T\frac{\partial t_{<ik>}}{\partial x_k} + \frac{5}{2}\bar\varrho\frac{k}{\mu}\bar T\frac{\partial\frac{k}{\mu}T}{\partial x_i} = -\frac{1}{\tau}q_i$$

$$\frac{\partial \varrho_{<ijk>}}{\partial t} - 3\frac{k}{\mu}\bar T\left(\frac{\partial t_{(<ij>}}{\partial x_{k)}} - \frac{2}{5}\frac{\partial t_{<r(i>}}{\partial x_r}\delta_{jk)}\right) = -\frac{9}{4}\frac{1}{\tau}\varrho_{<ijk>}$$

Navier-Stokes

$$\frac{\partial \varrho}{\partial t} + \bar\varrho \frac{\partial v_k}{\partial x_k} = 0$$

$$\frac{\partial v_i}{\partial t} + \frac{\frac{k}{\mu}\bar T}{\bar\varrho}\frac{\partial \varrho}{\partial x_i} + \frac{\partial \frac{k}{\mu}T}{\partial x_i} - \frac{1}{\bar\varrho}\frac{\partial t_{<ij>}}{\partial x_j} = 0$$

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

$$\frac{\partial t_{<ij>}}{\partial t} - \frac{4}{5}\frac{\partial q_{<i}}{\partial x_{j>}} - \frac{\partial \varrho_{<ijk>}}{\partial x_k} - 2\bar\varrho\frac{k}{\mu}\bar T\frac{\partial v_{<i}}{\partial x_{j>}} = -\frac{2}{3}\frac{1}{\tau}t_{<ij>}$$

$$\frac{\partial q_i}{\partial t} - \frac{k}{\mu}\bar T\frac{\partial t_{<ik>}}{\partial x_k} + \frac{5}{2}\bar\varrho\frac{k}{\mu}\bar T\frac{\partial\frac{k}{\mu}T}{\partial x_i} = -\frac{1}{\tau}q_i$$

$$\frac{\partial \varrho_{<ijk>}}{\partial t} - 3\frac{k}{\mu}\bar T\left(\frac{\partial t_{(<ij>}}{\partial x_{k)}} - \frac{2}{5}\frac{\partial t_{<r(i>}}{\partial x_r}\delta_{jk)}\right) = -\frac{9}{4}\frac{1}{\tau}\varrho_{<ijk>}$$

Cattaneo

$$\frac{\partial \varrho}{\partial t} + \bar\varrho \frac{\partial v_k}{\partial x_k} = 0$$

$$\frac{\partial v_i}{\partial t} + \frac{\frac{k}{\mu}\bar T}{\bar\varrho}\frac{\partial \varrho}{\partial x_i} + \frac{\partial \frac{k}{\mu}T}{\partial x_i} - \frac{1}{\bar\varrho}\frac{\partial t_{<ij>}}{\partial x_j} = 0$$

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

$$\frac{\partial t_{<ij>}}{\partial t} - \frac{4}{5}\frac{\partial q_{<i}}{\partial x_{j>}} - \frac{\partial \varrho_{<ijk>}}{\partial x_k} - 2\bar\varrho\frac{k}{\mu}\bar T\frac{\partial v_{<i}}{\partial x_{j>}} = -\frac{2}{3}\frac{1}{\tau}t_{<ij>}$$

$$\frac{\partial q_i}{\partial t} - \frac{k}{\mu}\bar T\frac{\partial t_{<ik>}}{\partial x_k} + \frac{5}{2}\bar\varrho\frac{k}{\mu}\bar T\frac{\partial\frac{k}{\mu}T}{\partial x_i} = -\frac{1}{\tau}q_i$$

$$\frac{\partial \varrho_{<ijk>}}{\partial t} - 3\frac{k}{\mu}\bar T\left(\frac{\partial t_{(<ij>}}{\partial x_{k)}} - \frac{2}{5}\frac{\partial t_{<r(i>}}{\partial x_r}\delta_{jk)}\right) = -\frac{9}{4}\frac{1}{\tau}\varrho_{<ijk>}$$

Grad´s 13-moment

$$\frac{\partial \varrho}{\partial t} + \bar\varrho \frac{\partial v_k}{\partial x_k} = 0$$

$$\frac{\partial v_i}{\partial t} + \frac{\frac{k}{\mu}\bar T}{\bar\varrho}\frac{\partial \varrho}{\partial x_i} + \frac{\partial \frac{k}{\mu}T}{\partial x_i} - \frac{1}{\bar\varrho}\frac{\partial t_{<ij>}}{\partial x_j} = 0$$

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

$$\frac{\partial t_{<ij>}}{\partial t} - \frac{4}{5}\frac{\partial q_{<i}}{\partial x_{j>}} - \frac{\partial \varrho_{<ijk>}}{\partial x_k} - 2\bar\varrho\frac{k}{\mu}\bar T\frac{\partial v_{<i}}{\partial x_{j>}} = -\frac{2}{3}\frac{1}{\tau}t_{<ij>}$$

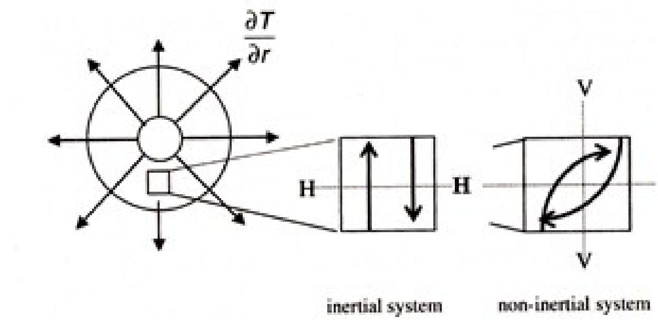
$$\frac{\partial q_i}{\partial t} - \frac{k}{\mu}\bar T\frac{\partial t_{<ik>}}{\partial x_k} + \frac{5}{2}\bar\varrho\frac{k}{\mu}\bar T\frac{\partial\frac{k}{\mu}T}{\partial x_i} = -\frac{1}{\tau}q_i$$

$$\frac{\partial \varrho_{<ijk>}}{\partial t} - 3\frac{k}{\mu}\bar T\left(\frac{\partial t_{(<ij>}}{\partial x_{k)}} - \frac{2}{5}\frac{\partial t_{<r(i>}}{\partial x_r}\delta_{jk)}\right) = -\frac{9}{4}\frac{1}{\tau}\varrho_{<ijk>}$$

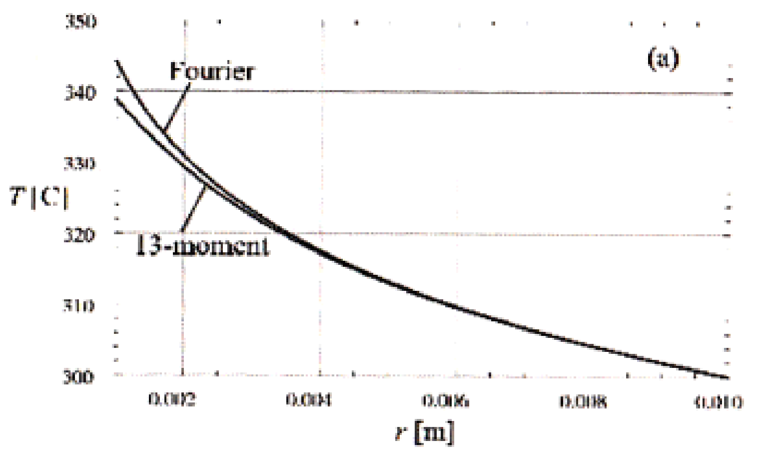
Heat conduction in the gap between two coaxial cylinders

Comparison between Fourier´s law and Grad´s 13-moment theory

H. Grad

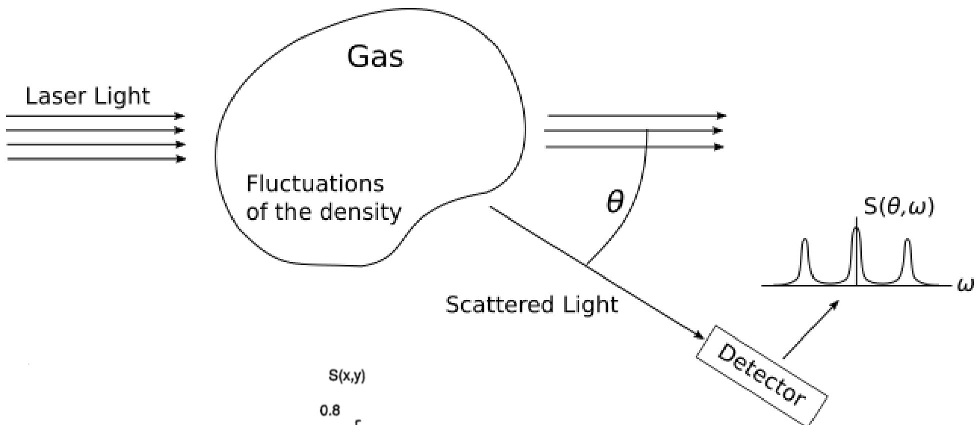


A gas cannot rotate rigidly between the cylinders, if there is heat.
A gas between the cylinders cannot be at rest on a turn table, if there is heat flow.

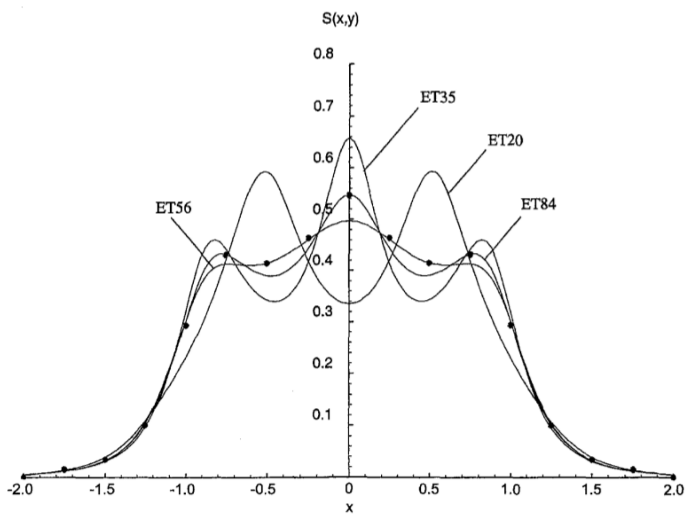


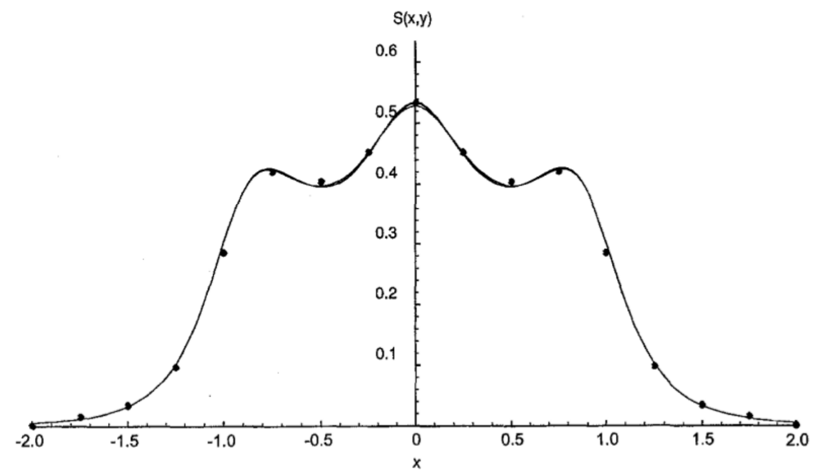
$$T = c_2 - \frac{c_1}{5\,{}^{k}\!/_{\mu}\, p\tau} \ln\left(r^2 + \frac{56\tau}{75p} c_1 \right)$$

Light Scattering



L. Onsager





ET 120, 165, 220, 286

ET is a theory of many theories with only one parameter: The number of fields.
For light scattering the theory provides results which are

- **satisfactory (because continuum theory works)**
- **surprising (because theory provides its own limit of applicability)**
- **disappointing (because so many moments are needed)**

Literature

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