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Readings in Statistical Mechanics, with commentaries.

These studies were undertaken in the Spring of 2011 anticipation of giving a series of lectures in the Wesleyan Physics Department. Despite the considerable amount of work evidenced in these notes, and certainly through no fault of his own, the project fell through.

I would be happy to give the lectures for a fee of $300 or more.

Dr. Roy Lisker

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From Ilya Progogine: "From Being to Becoming" WH Freeman 1981,

Chapter 2: The belief in strict determinism is only justified when the notion of a well-defined initial state is not an excessive idealization. Otherwise the concept of a world line must be replaced by that of ensembles of world lines.

Gibbs, Einstein: A representative ensemble is a cloud of points that is simplified into a continous fluid, with density $\rho= (q_1, \quad , q_s; p_1 ,.., p_s ; t)$. This "density" is fictive, but it allows one to make some sense of the otherwise ridiculous idea that a fluid can have an invariant "Liouville volume" fixed for all time, and a evolving "Boltzmann volume" that equals the exponentiation of the ever increasing entropy.

A "microcanonical ensemble" is one that is uniformly distributed on a constant energy surface

A "canonical ensemble" is a system in contact with a theoretically infinite energy reservoir, at unvarying energy T.

What are the conditions that must be imposed on the dynamics of a system to insure that the distribution function will approach either the microcanonical or canonical ensemble?

A system is "integrable" if there is a Hamilton-Jacobi transformation that transforms it into Action/ Angle variables, that is to say, constant first integrals and trigonometric expressions. These eliminate potential energy and have the simplified equations:

$$\boxed{\begin{array}{l} \varpi_i = \partial H / \partial J_i = d\alpha_i / dt \\ (dJ_i / dt) = 0\,;\ \alpha_i = \varpi_i t + \delta_i \\ q_j = (2mw_j J_j)^{1/2} \sin\alpha_j \end{array}}$$

Pages 7-15 If all systems were integrable, there could be no ***thermodynamic limit or approach to equilibrium*** **. The time invariant character of the J$_j$, fixes the long term behavior.**

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Gallavotti, Reiter, and Yngvason editors: "Boltzmann's Legacy" Conference lectures European Mathematical Society, c2008:

G. Gallavotti, E. Lieb, J. Lebowitz, C. Cercignani, GD Cohen, C. Villani, W Reiter and others

Pgs. 7-15, Giovanni Gallavotti: **The "proof" of the Equipartition Theorem in Boltzmann's paper of 1872 is only value for isochore transformations (no change in volume, hence Work =W= -pdV =0) and depends on the periodic motions of individual particles. A closed chamber of fixed volume, and with periodic motions.** ***The "equipartition theorem" follows*****: the uniform distribution in space will project uniformly onto any fixed energy surface.**

Boltzmann also assumes periodic motions for individual particles without collisions, then tries to cheat by saying that non-periodic motions are really infinite periods

Boltzmann looks for integral expressions that imitate or mirror thermodynamic quantities and their behavior, then goes on to assume that this is enough to make them the same things: qualitative similarity becomes quantitative identity!

To quote Gallavotti: ***"The thermodynamic analogies for small, simple systems transform into real thermodynamic relations for large complex systems"***

The fundamental relationship that he wants to preserve is

$$dS = (dU+pdV)/T$$

To justify this conflation of ideas, Boltzmann makes two assumptions, both of which are demonstrably false:

Assumption 1: **The** *Stoss- Zahl- Ansatz* **(density of collisions is the same everywhere, and uncorrelated** *before* **collision. The irreversibility then follows automatically from the fact that they cannot be uncorrelated after collision)**

Assumption 2: The Ergodic Hypothesis **(Molecules go through all possible states of motion. Or, time integrals equal space integrals.)**

Gallavotti, continued:

Boltzmann's fundamental paper of 1872:

(1) Identify absolute temperature (at equilibrium) with average kinetic energy per particle, over the periodic motion of a macroscopic collection of N identical particles

(2) Energy U = H(p,q)

(3) Pressure is created by collisions of particles on walls

Given these assumptions, p can be identified with the time average of the partial derivative with respect to volume of the energy. The fundamental equation then follows (this is well demonstrated in Fermi's book on Thermodynamics) Boltzmann's endorsement of the ergodic hypothesis is consonant with a picture of a "discretized phase space" Points are "cells" of finite size. Then the ergodic hypothesis implies a dynamic passage of the system through all the cells, as a 1-cycle permutation. "It is very doubtful that the dynamics of a gas has only one cycle". The hypothesis breaks down in computer simulations. Needless to say, "equipartition" becomes a triviality.

Gallavotti loosens up the ergodic hypothesis by the assumption

that it acts only on the "attractor" of the system. This has lower dimension , measure 0.

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Pgs. 16-20 Elliott Lieb

Foundations piled on top of foundations:

Thermodynamics is founded on Statistical Mechanics

Statistical Mechanics is founded on

1. **Newtonian Mechanics**
2. **Probablity Theory**

Probability is founded on Measure Theory

Measure Theory is founded on

1. **Topology**
2. **Geometry**

Topology is founded on Set Theory

Elliott Lieb: Stat Mech is based on 3 absurd notions:

The ergodic hypothesis is ridiculous

The equipartition assumption is ad hoc

The Stoss-Zahl-Ansatz is self-contradictory

Why, then, does statistical mechanics work?

Elliot Lieb continued , pg. 27:

Invokes two styles of doing physics

(i) Look at detailed interactions of particles

(ii) Look at large scale effects of particle interactions

The latter was Boltzmann'a approach: "Search for a function (any function) of the variables of phase space, that is continuous and differentiable (dx. dS, dE are well defined) and always increasing in time. In 1889 Poincare showed that there doesn't exist any function of the phase space variables that can do that.

A quote from JW Gibbs: *"The laws of thernodynamics are easily obtained from the principles of statistical mechanics, of which they are the incomplete expression."*

Boltzmann's insight: statistical ensembles lead to the Clausius Inequality.

Little Boltzmann Equation: $S = k_B \log W$. W is the area of the surface in phase space. It is assumed that the energy surface is discrete, and one uses "Boltzmann inflation"!

In the continuous limit:

$$\boxed{S = -k_B \int \rho \ln \rho dq_1 ... dq_n dp_1 ... dp_n}$$

Where ρ is the probability density in phase space. When applied to quantum mechanics the formula becomes $\boxed{S = -k_B Trace(\rho \ln \rho)}$

20th century developments are a major departure from Boltzmann:

(a) Specific heats are suppressed relative to classical values

(b) Superfluidity, super-conductivity, Bose-Einstein condensates are contrary to the assumption that the world becomes more chaotic with time

(c) Contrast of gravitational degrees of freedom, radiative degrees of freedom, and the collisional degrees of freedom lead to very different ways of looking at Entropy over time.

(d) The literal use of the Boltzmann entropy expression

$$\boxed{\rho \propto Exp(-H / k_B T}$$

gives a value of - ∞ for entropy at absolute zero. This means that quantum mechanuics and the von Neumann trace matrix must be brought into play.

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Joel Lebowitz:

Many conceptual and mathematical problems involved in the passage from a time-symmetric Hamiltonian at the mictoscopic level, to a time asymmetric diffusion equation at the macroscopic level.

(1) ″Atoms are simplified to the point of caricature″.

Quote from Feynman: "(Atoms are) particles in perpetual motion that repel when squeezed″

(2) Irreversibility

(3) Coarse Graining. Notion of a "density″ that makes sense only when phase space is divided into indivisible cells.

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Commentary by Roy Lisker

Statistical Mechanics is in the best traditions of theoretical physics, and Boltzmann was a genius in that tradition. There is a 6-step procedure:

Step 1: **One accurately describes a phenomenon empirically which is not understood theoretically . (Eg. The mathematics of thermodynamics, which is really a description, not a theory)**

Step 2: **A model is proposed**

Step 3: **Lousy mathematics uses the model to derive pre-existing formulae presented in step 1**

Step 4: **The mathematics is used to make predictions, which exposes its limitations**

Step 5: **The mathematicians come in and clean up the mathematics**

Step 6: **The process advances BOTH physics and mathematics.**

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A short list of the absurdities in the standard models for Stat Mech:

1. **"Density" of a "perfect *massless* fluid"**
2. **Passage from a massless fluid of discrete particles, to a**

continuous fluid, uncountably many points forming a continuous volume. Counting is replaced by measure theory

(3) Confusion between "ensemble" picture of Gibbs, and "configuration space" world-line of Boltzmann . To address this confusion, Boltzmann invents the "ergodic hypothesis"

(4) After the fluid has been rendered continuous, the phase space itself is "discretized"!

(5) Yet, to make the probability work, a measure is applied to phase space, although measures are of necessity continuous.

Summarizing the bad mathematics

(1) The ergodic hypothesis

(2) Equipartition of energy

(3) Stoss-Zahl-Ansatz (molecular chaos)

(4) Treating the micro-canonical ensemble as a continuum

(5) Discretization of phase space

(6) Reversion to a continuum model for the phase space, so that one can get the Maxwell-Boltzmann distribution

(7) The density of states

(8) Criterion for "equivalence" of microstates in the macrostate

(9) Loschmidt reversibility paradox

(10) Poincare and Zermelo recurrence paradoxes. H-functions can't be constructed.

Quote, Gibbs: *"The (postulate of) the impossibility of an uncompensated decrease of Entropy seems to have been reduced to an impossibility."*

Joel Lebowitaz, pg 70: This discussion should be read in conjunction with the paper by Sergio B. Volchan : Probability as typicality ***http://arxiv.org/abs/physics/0611172***

Probabilistic "typicality" is central to the Gibbs ensemble paradigm: All microstates ***with the same 'typicality'*** **in their probability are amalgamated to the same macrostate. This is used to cover over the sheer impossibility of giving a precise "probability" to each microstate.**

Applying this notion to differing perspectives of Gibbs and Boltzmann:

***Gibbs:* The phase space volume 'spreads out" like a liquid (ink squirted into a glass of water), over the total phase space**

***Boltzmann:* A individual trajectory in phase space (of trillions of dimensions) covers the whole phase space in such a manner that it spends almost all of its time in the "typical" rather than the "rare" boxes.**

The Gibbs Paradigm

(1) Begin with a container, like a cylinder, holding 10^{20} "particles". (Recall that the atomic theory did not win acceptance until late in the 19th century. These "particles" are already a discretization)

(2) Make this into a single point in a 10^{20} dimensional Configuration Space .

(3) Create a continuous ensemble of systems with all possible initial

conditions , that is to say, all possible energy distributions (momenta are considered less significant), under the constraint of a fixed total energy E, (*or a pizza slice of energies between E and E+dE*).

(4) Estimate the most typical outcome of the expansion of this fluid into a larger enveloping cylinder, in a length of time t under Hamiltonian collision dynamics (*which of course do involve momenta, another mathematical anomaly.*)

(5) By Liouville's Theorem, the volume of the fluid doesn't change, as it "thins out" over the enlarged phase space VC_2 from the initial cylinder VC_1 ,

(6) However, although we've worked with the fiction of a continuous fluid, enabling us to use the Liouville Theorem, we now discretize the phase space, to invent a fictive volume obtained by adding up the number of cells that receive even one particle from the fluid.

Here, quantum theory helps, and one can give a minimal size to the side of a typical cell in W, that is, it must be proportional to h. Thus h is at the intersection in Nature, where the Second Law goes

over into the Uncertainty Principle. Therefore, Quantum Theory is required to save even the most fundamental of all State Mech equations $S = k_B \ln W$.

(7) The crucial difficulty is the *Stoss-Zahl-Ansatz* : namely, that all of the microstates (cells of the phase space), have the same "likeliness" before the process begins (hypothesis of molecular chaos, ergodic equipartition). This diminishes with time.

One now argues that the various permutations of a microstate all belong to the same macrostate. (These permutations remaining within the same set of locations. These increase with the opening of cylinder one into cylinder two) Simply stated, the fewer the symmetry principles the higher the typicality.

By maintaining the ambiguity between the discrete and the continuous, one introduces Measure Theory and argues that the volume of special states has measure 0.

(8) The criterion of 'typicality" is the Maxwell-Boltzmann distribution of energies combined with a completely uniform spatial distribution.

(9) It is now assumed, rather grossly, that a fluid of constant Liouville volume will typically cover *all* the cells of the new phase volume. The special states are those which cover only part of the new phase volume. But this makes nonsense of the Liouville volume notion.

(10) Summarizing: maximal typicality has two features:

(a) Uniform distribution of particles (every cell has the same number of "particles".

(b) Maxwell-Boltzmann distribution of energies *within* each cell! (The number of particles (cells?) with energy k = ½ v^2 , is given by

(11) $$f_\epsilon(\epsilon)\,d\epsilon = \sqrt{\frac{\epsilon}{\pi kT}}\ \exp\left[\frac{-\epsilon}{kT}\right]\,d\epsilon$$

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Joel Lebowitz continued pg 75:

Cosmological considerations: the eternal problem of the "initial state of the universe". It must have had vanishingly small entropy. But this seems to contradict the concept of a totally chaotic Big Bang.

Roger Penrose's Solution: **Low entropy for gravitational degrees of freedom means a uniform distribution of matter. High entropy is manifest in clumping**

Low entropy for random motion (gaseous, inertial, not gravitational, Gaussian distribution of velocities) means uniform motion. High entropy means chaotic or Maxwell-Boltzmann distribution. Likewise for radiation.

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Carlo Cercignani, in the Gallavotti Antology

(1) Boltzmann's H-Theorem paper of 1872. There are two interpretations of the distribution function:

(a) The fraction of a 'sufficiently long" time interval during which the velocity of a *specific molecule* **has values within a certain volume of momentum space**

(b) The proportion of molecules which, at a specific instant, have

a certain velocity within a narrow range of velocities. Boltzmann eventually realized that these were not equivalent and came up with the Ergodic Hypothesis: the position and momentum of every molecule eventually take up all possible values compatible with the given total energy.

Ehrenfest's assumption: **$T = k_B$(average of K.E. perm atom) . This is only true for perfect gases and solids at room temperature.**

List of assumptions in the Boltzmann Picture:

a. **Molecules are hard, perfectly elastic spheres.**
b. **If the "state (p,q) is known with perfect accuracy, they can be reduced to points.**
c. **Otherwise one invokes the probability distribution: let the density be given by D=f(x,x, t); f_0 = f at time t =0. Then**

$$\boxed{df/dt = G - L = \partial f/\partial t + \xi \bullet \partial f/\partial x}$$

The "Ldxdξdt" term, gives the expected number of particles

passing out of a "cell" because of a collision. Gdxdξdt gives the number that enter. Obviously both are finite-usual uneasy back and forth between density and number. The end result is (H-Theorem paper of 1872):

$$\boxed{\begin{array}{l} {}^{\partial f}\!/_{\partial t} + \xi \bullet {}^{\partial f}\!/_{\partial x} = \\ N\sigma^2 \int_{R^3}\int_{B} (f(x,\xi',t)\, f(x,\xi_1',t) - f(x,\xi,t)\, f(x,\xi_1,t))(\xi_1 - \xi) \bullet n d\xi dn \end{array}}$$

List of hidden assumptions:

(1) Stoss-Zahl-Ansatz. Although this must be present initially. It is immediately destroyed by the interactions. However, it is argued that "it is only needed for molecules which are about to collide. However : "It is very hard to to prepare an initial state in which chaos does not hold."

One cannot, however, have non-correlation both before *and* after a collision. This is the Loschmidt argument against the H-Theorem.

In fact, according to Cercignani, the H-theorem seems to have a very limited validity, and is only used in studying the properties of dilute gases.

Since 2000 the Boltzmann equations have been the basis for extensive mathematical investigation and a search for rigorous solutions.

(i) 1933 Proofs of Existence and Uniqueness for gas of hard spheres (Thespace is homogeneous, dependency on velocity and time, but not on position)
(ii) 1949 Harold Grad's theorems . Use of orthogonal polynomials
(iii) Lanford's famous theorem. Deriving Boltzmann

irreversibility from reversible mechanics under very restrictive conditions.

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E.G.D. Cohen, from the Gallavotti Anthology **: Entropy, Probability, Dynamics**

Boltzmann's papers:

(a) 1872, Mechanistic approach

(b) 1877, Probability approach. This may have been influenced by the criticism from Loschmidt. The formula S= klnW comes from a paper of 1887, and only applies to an ideal gas in thermal equilibrium.

Now a new idea, different from "typicality" or "likeliness" appears: "complexions. Complexions are an additive progression of discrete energies ε, 2ε, …These are hypothesized to be invariant both before and after collisions. Each distribution of total kinetic energy is a "complexion". The number of molecules with energy jε is designated as ωj. Then the number distinct energy distributions, P, that one wants to maximize is given by

$$\boxed{P = \frac{N!}{\prod_{j=1}^{q} \omega_j!}}$$

One employs basic combinatorics to derive the partition function.

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Erwin Schrodinger: "Statistical Thermodynamics" Cambridge UP 1964 .

Using Stirling's formula, one quickly derives

$$\boxed{\varpi_s \sim Exp(-\frac{s\varepsilon}{(E/N)});}$$

One method covers all forms of statistical physics, whether classical, quantum, Fermi-Dirac, Bose-Einstein, etc.

The principle problem in statistical thermodynamics is the distribution of a given amount of energy E, over a huge number of identical systems, atoms, molecules ,quanta.

A related, secondary issue: distribution of N identical systems over all possible states, given a fixed amount of energy E.

One disregards the interaction energy, gravitation, etc. This allows one to speak of an absolute energy per particle which is not shared.

Momentum is not considered, which is strange, since the motor of change is via collisions.

The standard sophistry: From one end: describing those features which are common to all possible states of the assemblage, which therefore "almost always" obtain.

From the other end: Those little boxes each with their single state. This creates two different attitudes towards the mathematical application to the physical results.

Attitude 1: **N existing physical systems in real physical interaction.(electrons, gas molecules, Planck oscillators). This viewpoint only works with gases. There must be many identical constituents, and violates the very notion of a solid**

Attitude 2 *(Willard Gibbs):* **N identical systems are mental copies of the one system. What, then, does it mean to distribute energy over N systems? We are free to regard any one of these systems as the one actually under observation**

Consider N identical systems. The list of possible energy eigenvalues is

$$\boxed{\begin{array}{l}\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_l, \ldots \\ \varepsilon_{l+1} \geq \varepsilon_l\end{array}}$$

If the system is classical, it is completely determined once one knows that S_1 is in state l_1 , S_2 in state l_2, etc. This isn't true for quantum statistics which invokes probability amplitudes Each state has an "occupation number", a_j , which gives the number of electrons in a given state.

$$\boxed{\begin{array}{l}P = \dfrac{N!}{a_1!a_2!\ldots a_l!\ldots} \\ \sum a_l = N; \sum a_i\varepsilon_i = E \\ \dfrac{E}{N} = \dfrac{\sum a_i\varepsilon_i}{\sum a_l}\end{array}}$$

Boltzmann observed that the maximum for P is astronomically much larger than any lesser value. This can be shown rigorously for $N \to \infty$. However, when N becomes small one must pay attention to the fluctuations of Brownian motion. The standard treatment now follows.

To maximize *ln* P, we use the technique of Lagrange multipliers to the expression :

$$\boxed{A = \ln P - \lambda N - \mu E = \ln N! - (\sum \ln a_i!) - \lambda(\sum a_i) - \mu(\sum \varepsilon_i a_i)}$$

All of the a_i's are treated as if they were continuous, autonomous variables, although in fact they are integers. A better approach therefore would be to use the ratios of the a_i's to N, which, in the limit can be approximated as continuous variables. In any case, one invokes a crude approximation of Stirling's Formula, *then* takes the derivative:

$$\boxed{\ln k! \approx k(\ln k - 1)}$$

$$\boxed{\begin{array}{l} A \approx \ln N! - \sum a_l(\ln a_l - 1) - \lambda(\sum a_i) - \mu(\sum \varepsilon_i a_i) \\ \partial A \big/ \partial a_l \approx -\ln a_l + 1 - 1 - \lambda - \mu \varepsilon_i \end{array}}$$

Hence

$$\boxed{\ln a_l + \lambda + \mu \varepsilon_l = 0}$$

Solving for each a_l gives :

$$\boxed{\begin{aligned} a_l &= e^{-\lambda-\mu\varepsilon_l} \\ N &= \sum e^{-\lambda-\mu e_l} \\ E &= \sum \varepsilon_l e^{-\lambda-\mu e_l} \end{aligned}}$$

These are the basic formulae of of Stat Mech, from which the quantities of Thermodynamics, and the partition function, are derived. The partition function is the expression for E/N.

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Commentary

Mathematically this procedure is outrageous!! **The a_j's are huge integers, one can hardly speak of "differentiating". In the Stirling formula, these extremely discrete functions making huge leaps are replaced by an "asymptotically continuous" function, with meaningless infinitesimal increments producing controllable increases on the range.**

Then, worse still, one applies Langrangian Multipliers! Obviously there are othe means to the same results, but the procedure is ..well… absurd!

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$$U = \frac{E}{N} = \frac{\sum \varepsilon_l e^{-\mu e_l}}{\sum e^{-\mu e_l}}$$

$$= -{}^{\partial(\ln(\sum e^{-\mu e_l})}\!\Big/_{\partial\mu}$$

Clearly one can get rid of λ .

$$\lambda = -\ln a_l - \mu\varepsilon_l$$

***The multiplier μ turns out to be the temperature*. This is not surprising as its inverse is the integrating factor for dQ. To demonstrate this, Schrodinger imagines the interaction of two quantities of perfect gases, A and B. He (somewhat arbitrarily) assumes that the energies of the new mixture e_k , are arbitrary sums of the energies of the old, α_m, and β_n : $\varepsilon_k = \alpha_m + \beta_n$ .. Then he shows, or claims to, that if the μ of the first mixture = μ of the other mixture, their interaction produces no work, because the μ of the combination will also not change. He also shows that 1/μ is the integrating factor . The specific equation, which is easily seen to be the basic equation of thermodynamics in disguise, is**

$$\mu = F(T) = \frac{1}{kT}$$

$$d(F + U\mu) = \mu(dU - \frac{1}{N}\sum q_l d\varepsilon_l)$$

The expression on the left is the "free energy". Substituting in previous formulae gives the classical form of the Partition function:

$$Z = \sum e^{-\frac{e_l}{kT}}$$

The free energy is given by

$$F(T) = -k\ln Z = \frac{U - ST}{T}$$

Thus:

All of thermodynamics comes from the Free Energy and the Partition Function.

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From Fermi's Thermodynamics

Even the term "state" means different things in Thermodynamics and Statistical Mechanics. The *equation of state* in Thermodynamics connects pressure, volume and temperature F(p,V,T) =0. The normal procedures is to make a Cartesian system of two of these variables, then draw isobars of the third variable, or some quantity compounded from them , "isothermals", "isochrores", etc.

(1) homogenous system is mixture of several compounds, with a "global" equation of state.

(2) A nonhomogenous system has several compounds each with its own state equation.

(3) Systems with moving parts. In thermo (not in stat mech) one neglects the kinetic energies of the moving parts. The values of these kinetic energies (see Schr) are the "states". Thus, an infinity of "states" of molecular motion may correspond to a single thermodynamic state. Hence the origin of the *ensemble* approach of Gibbs.

Equilibrium "states". Systems transform from an initial state to a final state through a continuous succession of infinitesimal intermediate states. This is the origin of all the headaches felt by physicists and mathematicians, albeit for different reasons.

Example: **reversible expansion of a gas. Enclose gas in cylinder with piston, raise or lower piston infinitely slowly! (Since the basic equation of Thermodynamics is a total indifferential (hah!), this eliminates the pdV , or work term, and just leaves the heat.**

Cycles. **The work done by a cycle is the area enclosed in the loop, in the (p,V) plane in the Carnot process (lifting and lowering pistons, moving cylinders to infinite heat soruces at fixed temperatures) .**

For a "perfect dilute gas", the equation of state is $pV= (m/M)RT$

R is the "gas constant"= 8.314×10^{7} erg/degrees = 1.986 Cal/degrees

m is the number of grams of gas; M is the molecular weight of the element or chemical (e.g. water)

A gram-mol is a weight whose numerical value, in grams, is equal to the molecular weight of the substance. Thus, $m/M = 1$ for any gram-mol.

Density π = m/V = pM/RT. For an *isothermal expansion*, one has dT=0, and

$$L = \int_{V_1}^{V_2} p\,dV = ({}^{m}\!/_{M})RT\int_{V_1}^{V_2}\frac{dV}{V}$$
$$= ({}^{m}\!/_{M})RT\ln({}^{V_2}\!/_{V_1}) = ({}^{m}\!/_{M})RT\ln({}^{p_2}\!/_{p_1})$$

In a mixture of gases, the partial pressure of a component is the pressure that this component would exert if it alone filled the container. Dalton's Law: The pressure of a mixture of gases is the sum of its partial pressures

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Georg Joos: Theory of Heat

The small calorie is the amount of heat required to raise the temperature of one gram of water from 14.5° to 15.5° Centigrade. The large calorie is the amount needed to raise 1 kilogram of water from 14.5° to 15.5° .

Specific heat: **the amount of heat that raises a gram of a specific substance by 1 degree.**

Molecular heat : the amount that raises one mol of the substance by one degree.

Okay: here is the basic calculation for finding the "intermediate heat" when quantities of two substances at different temperatures are brought together. For example q_s of substance S at temperature T_s is brought into content with q_w of another substance at temperature T_w . If the specific heats of S and W are c_s, then

$$q_s c_s T_s + q_w T_w = (q_s c_s + q_w c_w)T$$
$$T = \frac{q_s c_s T_s + q_w T_w}{(q_s c_s + q_w c_w)T}$$

"Heat transferred from one body equals heat absorbed by the receiving body"

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Back to Fermi:

The First Law of Thermodynamics

This is simply a restatement of the conservation of energy for thermal systems. The assumption is that the variation of energy must equal the amount of energy received from the external environment.

Hence the use of the minus sign –L, as the work "performed" by the system. If A and B are two states of a system, then $-L = U_B - U_A$ is the work performed "by" the system, which is –the work "on the system. Work is a total differential, and path independent .

An example of "two ways" of going from A to B (Water to Steam)

1. **Heat water on flame to raise temperature from A to B. The volume changes very little, and one says there is no "work" done on the system.**
2. **Use rotating paddles on central to heat by friction. In this case mechanical work was used to keep the paddles moving.**

   Example 2, basically the Carnot Cycle

   (1) S is a cylindrical container, perfectly insulated. Bring in a moving piston. This changes the volume

$$\Delta U = U_B - U_A = -L$$
$$\Delta U + L = 0$$

If the insulation is not perfect, $\Delta U + L = Q$ is the amount of energy received by means other than mechanical work. It is a leap of speculation

for Boltzmann to claim that this comes from the agitation of molecules or atoms. For a "cyclic" transformation ΔU = 0: "The work performed by the system equals the amount of heat absorbed by the system" That is the Carnot cycle. We can now derive the basic equations of Thermodynamics:

$$dQ = dU + pdV$$

$$dU = (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV$$

$$dQ = pdV + \{(\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV\}$$

$$= dV(p + (\frac{\partial U}{\partial V})_T) + dT(\frac{\partial U}{\partial T})_V$$

One can also take p and T as the independent variables. Then

$$dQ = dU + pdV$$

$$dU = (\frac{\partial U}{\partial T})_p dT + (\frac{\partial U}{\partial p})_T dp$$

$$dV = \{(\frac{\partial V}{\partial T})_p dT + (\frac{\partial V}{\partial p})_T dp\}$$

$$dQ = dT((\frac{\partial U}{\partial T})_p + (\frac{\partial U}{\partial p})_T) + dp((\frac{\partial U}{\partial p})_T + p(\frac{\partial V}{\partial p})_T)$$

Finally, one takes V and p to be independent variables. Then

$$dQ = (\frac{\partial U}{\partial p})_V\, dp + dV((\frac{\partial U}{\partial V})_p + p)$$

Definitions: **Thermal Capacity is given by dQ/dT . There are two thermal capacities depending on whether heating is done under constant volume, or constant pressure:**

$$C_V = (\frac{\partial U}{\partial T})_V = (\frac{dQ}{dT})_V$$

$$C_p = (\frac{\partial U}{\partial T})_p + p(\frac{\partial V}{\partial T})_p = (\frac{dQ}{dT})_p$$

Making Thermodynamics palatable to the mathematician

(1) Work, heat, entropy are quantities in transitions or transformations

(2) Because they are measured in "equilibrium states", they are presented as infinitesimals. This is the basis of thought experiments in which processes move with infinite slowness. (Call up Zeno!)

(3) Basic equation is dQ=dU+pdV . - L is work done on the system, L is work done by the system.

(4) dU and dV are total differentials in variables p,V, T. It is customary

to let V be the dependent variable, because p, T are active. V being a measure of empty space is treated as passive.

(5) dQ is not a total differential. To evaluate the integral that calculates the quantity of dQ one must have a trajectory on the (p,T). Essentially one can then express both parts as a function of temperature.

(6) 1/T is an integrating factor. Thus , S = dQ/T is a total differential. One relates U to T by the hypothesis, a quasi-theorem, that defines temperature as the particle average of the total energy. Then if

(7) $dQ/T = dU/T + fdV/V = NdU/U + kd(\ln V) = d(\ln U^N V^k)$

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Page 164: Fermi's derivation of all the properties of entropy, using the model of the Carnot cycle. All we need from this is the derivation of the fundamental integral (which figures in the H-theorem) $\oint \frac{dQ}{T} \leq 0$

Fermi on Entropy , quote: "In an isolated system, the statistically significant transformations occur take the system to a state of higher probability"

It is easily shown that the sum of entropies is given by the product of probabilities $S = k\ln W$. $k = R/A$ = Gas Parameter/Avogadro's Number

Going back to our definitions of thermal capacity, if CV is fixed, then

$S=C_V\ln T + R\ln V + a$ (constant of integration) $= \ln T^{CV}V^{Ak}$

IF Cp is constant, we get

$S=C_p\ln T - R\ln P + R\ln R$

Putting these together, one derives the important formula

$$(\frac{\partial U}{\partial V})_T = T(\frac{\partial p}{\partial T})_V - p$$

The van der Waals Equation

The ideal gas law $pV = kT$ works well for high temperatures and low pressures, or high volumes. The van der Waals law is a correction for gases near their condensation points. It takes into account the size of the molecules and the cohesive forces between them.

The gas law is modified as follows: $(p + a/V^2)(V-b) = RT$

a and b are characteristic coefficients for specific substances. b is a function of the size of the molecule, while a/V^2 reflects the cohesive forces.

We look at the "critical point of inflection, C", or so-called labile states of very high pressure before condensation sets in.

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Cedric Villani: "A review of mathematical topics in collisional kinetic theory" Handbook of Mathematical Fluid Dynamics (Vol. 1), edited by S. Friedlander and D. Serre, Elsevier Science (2002).pgs 71-305

The subject of Villani's treatise is *Collisional Kinetic Theory*, a branch of Non-equilibrium Statistical Physics. It is based on a small number of famous mathematical models. There is more emphasis on methods and ideas than on results. Fully non-linear theories are more common than perturbative approaches.

Chapter 1

The Distribution Function

"The object of kinetic theory is the modeling of a gas (or plasma) by a distribution function in the particle phase space"

Single species of particles, non-quantum, non relativistic. The macroscopic variables are positions, the microscopic are velocities. Consider the gas to be contained in a domain X in 3-space, in a time interval (0,T).D= density = f(t,x,v) is the distribution function. F is a function of bounded measure for any compact subset of X. In physical space, the domain is assumed to contain a finite amount of matter. There are two ways to interpret f

1. **As an approximation of the true density in phase space**
2. **As a probabilistic strategy for dealing with our lack of knowledge**

The Kinetic approach was created by Benoulli and Clausius long before the experimental evidence for the existence of atoms.

The Fundamental Ansatz :

ALL measurable macroscopic quantities can be derived from microscopic averages.

(*Comment:* **This doesn't say anything about the causal mechanisms, how one gets from the molecules or atoms to the**

measurable phenomena. Different pictures could give different results)

Variables: x, t, v , T , density ρ . Then :

$$\rho = \int_{R^3} f(t,x,v)dxdtdv$$

If x and t are fixed, this becomes an integral of the single variable ,v. We express the equipartition and conservation equations as follows. Let u be the fixed velocity, v the variable under the integral sign. Then

$$\rho u = \int_{R^3} vf(v)dv$$
$$\rho\left|u^2\right| + N\rho T = \int_{R^3} \left|v^2\right| f(v)dv$$

The "transport operator". The assumption is that the "density" propagates without compression, expansion or change. This is, in essence, Liouville's Theorem: f(t,x,v) =f(0, x-vt,v) x and v are of course abbreviations for 3-tuples. The total time derivative of f can be broken into a temporal part and a gradient:

$$D_t f = {\partial f}/{\partial t} + v \bullet \nabla f = 0$$

The gradient part is what is known as the "transport operator". If there is a macroscopic force, F, then this equation is given a Newtonian modification as:

$$D_t f = \partial f / \partial t + v \bullet \nabla_x f + F \bullet \nabla_v f = 0$$

Only binary collisions are considered: 3 or 4 particle collisions are considers too rare to bother with. The model used here will be that of "hard, elastic spheres" with radii r, $nr^2 \sim 1$, $nr^3 \leq 1$, where n is the number of particles .

The 5 assumptions:

1. **The gas is dilute**
2. **Collisions are very brief events at very precise locations ,x .**
3. **Collisions are assumed perfectly elastic. Therefore**

   Velocities before collision v', v'_*

   Velocities after collision v, v_*

$$v^2 + v_*^{\ 2} = v'^2 + v_*'^2$$

$$v + v_* = v' + v_*'$$

Then $$v' = \frac{v+v_*}{2} + \frac{|v-v_*|}{2}\sigma$$

$$v_*' = \frac{v+v_*}{2} - \frac{|v-v_*|}{2}\sigma$$

σ is the "deflection angle", σ = sinθ

(4) Everything is microreversible

(5) Molecular chaos (*Stoss-Zahl-Ansatz!*) *"The velocities of particles before collision are uncorrelated"*

When Boltzmann realized that it could not continue to apply after collisions, he invented the Ergodic hypothesis.

Using these 5 assumptions, Boltzmann derived the Quadratic Collision Operator, which we will write out in full:

$$v^2 \frac{\partial f}{\partial t} = D_t f - v \bullet \nabla_x f = Q(f, f)$$
$$= \int_{R^3} dv_* \int_{S^2} B(v - v_*, \sigma)(f' f_*' - f f_*) d\sigma$$

As a general rule, the kernel, B, is not integrable. The flux term in f,which is a tensor product in probabilities, is allowed because the

particles are uncorrelated before collision. Even though they are no longer uncorrelated after collision, Boltzmann continutes to use the same expression. This in essence is the Loschmidt objection.

Here is how the 5 assumptions go into the integral and the theorem

1. **Only binary collisions are assumed**
2. **t and x are treated as parameters, that is to say, the collisions are localized in time and space**
3. **Collisions are perfectly elastic, as required for the tensor product**
4. **The microreversibility is built into the structure of the kernel B**
5. **Stoss-Zahl-Ansatz**

Note that Df is linear, while Q(f,f) is non-linear

Here Villani goes into a discussion of several traditional potentials that produce the kernel B. A general classification of collision kernels:

A. Artificial collision kernels. No corresponding phenomenon in nature, but useful for making calculations

B. Cut-off kernels. Replace kernel by another that is locally integrable

C. Variable hard spheres

D. Condition of specular reflection (Fermat)

E. Maxwell diffusion. A special Gaussian distribution found only at the wall

F. Linearized Boltzmann equation, etc.

As for the physical validity of the H-Theorem equation, it works only in dilute atmospheres, for example aeronautics at high altitudes, or interactions in dilute plasmas.

Both Loschmidt and Poincare can be ignored in an appropriately small box of phase space and time, (*Comment:* That's like saying the earth is flat provided one stays within a 2 block radius)

Although there are 3 kinds of kernels (hard spheres, oscillators and incompressible fluids), the mathematical theory has been developed only for the hard sphere case.

Harold Grad's work begins with Newton. His theorems were not shown to be consistent until 1972, by Cercignani.

The Harold Grad approach

Hard spheres of radius r. Billiard reflections, “symmetrical densities”: particles are ‘indiscernable though at a distance r from each other.” The Flow St on the hard spherical particles induces a “flow on the probabilities”. Take the continuum limit n →∞, r ~√(1/n) Boltzmann –Grad assumption: f becomes continuous as the number of particles becomes sufficiently large. Also, as n goes to infinity, the motions of the particles becomes independent, t hat is to say, uncorrelated.

With these assumptions, one can show that the limit function of the process Pf^n is a solution of the Boltzmann equation.

Landford’s Theorem: **This proves the Boltzmann equation and relations for very short time intervals and strong assumptions on the iterations P^kf^n . These are:**

(i) F is “continuous”

(ii) Gaussian type limits

(iii) Uniform convergence of $P^kf_0^n$.

(iv) Chaos assumption

The arguments are exceedingly vague. Notion of "most likely" distribution is basically the same as the Stoss-Zahl-Ansatz.

We say that z is "admissible" if $W_z = \frac{1}{n}\sum_{i=1}^{n}\delta(x - x_i, v - v_i)$ **is a "good approximation to the density function f(x,v)dxdv. Then** f^n **will be "arbitrarily close" to the tensor product** $f^{\otimes n}$**in the sense of the "weak convergence of the marginals" . This condition is not sufficient to derive the Boltzmann equation.**

Then there is the "problem of the localization of collisions"

Summarizing the mathematics:

Assume that f_t^n **can be derived from** f_0^n **by transport under the mechanisms of microscopic dynamics. Let** μ_t^n **be a probability measure, with density** f_t^n **. Then, for all bounded, continuous f(x,v) on** $R_x^3 x R_v^3$**, we have :** $\mu_t^n = \int \varphi(x,v)(W_z - f_t(x,v))dxdv \to 0$ **, where** f_t **is the saolution to the Boltzman equation with initial f0 and the z operates only on the**

"admissible points" . This means that "unlikely configurations" could lead to very bad approximations. (Landford 1973)

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From Stephen Brush: "The Kinetic Theory of Gases: An Anthology of Classic Physics" Imperial College Press 2003

Outline of Boltzmann's H-Function paper of 1872

Boltzmann constructs the following integrals

$$Q(f,f) = \int_{R^3} dv_* \int_{S^2} B(v - v_*, \sigma)(f' f_*' - ff_*) d\sigma$$

$$\int Q(f,f)\psi dv = \int dv \int_{R^3} dv_* \int_{S^2} B(v - v_*, \sigma)(f' f_*' - ff_*)\psi d\sigma$$

$$\psi = \ln f$$

$$\int Q(f,f) \ln f dv = -Df$$

By an (excessive!) series of manipulations involving changes of variables and integration by parts, which could certainly have been simplified and takes up many pages, Boltzmann arrives at:

$$\int D(f)dt =$$

$$\tfrac{1}{4}\int\int\int dv dv_* d\sigma B(v - v_*)(f' f_*' - ff_*) \ln\left(\frac{f' f_*'}{ff^*}\right)$$

Note that the integrand is of the form (X-Y)(lnX-lnY). Assuming that the kernel is positive, this means that the integral will always be > 0 . Therefore the derivative will be positive, and the quantity D will always be increasing.

Commentary

Boltzmann therefore:

(1) Identifies D with the entropy

(2) Assumes that it rises to a maximum

(3) That this will happen in finite time

(4) Assumes that the integrand is continuous, and therefore that D is differentiable

(5) Assumes that this maximum is stable, that is, there will not be jumps along the way

(6) Assumes that the maximum is a finite number

(7) Argues that the distribution at the unique critical point will be the Maxwell-Boltzmann distribution derived from the equipartition of energies.

Putting everything together:

$$f = f(x,t,v)$$

$$H = \int f \ln f dx dv$$

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + v \bullet \nabla H = -\int D(f,x) dx$$

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Brush Anthology, continued

James-Clerk Maxwell papers of 1866-68

The assumption in these is that molecules behave like point centers of force mean values of various functions of velocities, and variations around these mean centers. Only collisions are considered, no external forces, gravity, diffusion, etc.

"Now we know that in fluids the elasticity of form is evanescent, that of volume is considerable" He invokes a cardinal principle of elasticity "Forces caused by small changes in form are proportion to these caused by small changes in volume".

Gives up on a theory based on elasticity of stationary molecules, goes on to consider moving molecules. Dynamic theory: molecules oscillating around a fixed location.

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Harvey R. Brown, Wayne Myrvold: "Boltzmann's H-Theorem, its limitations and the birth of (fully) statistic mechanics".
www.philsci-archive.pitt.edu/4187/

Boltzmann's 1872 H-Theorem paper : Gas composed of hard spherical molecules. The container has perfectly elastic walls. Only binary collisions considered. To be precise: Boltzmann claims that he is working with perfect Euclidean points, but in fact the treatment uses hard elastic spheres.

Boltzmann's Transport Equation. Assumes isotropic. This means that $\partial f / \partial t$ **depends only on collisions that alter v.**

Harvey Brown invokes a particular form of the Stoss-Zahl-Ansatz . This turns out to be equivalent to $F(v_1, v_2, t) = f(v_1, t) f(v_2, t)$ **where F is the density of those pairs of molecules which are destined to collide within the period (t, t+Δt).**

The "H-functional" is defined as

$$H = \int f(x,v,t) \ln\, f(x,v,t) d^3 rd\ \ v$$

Criticisms of Loschmidt, Poincare and Zernelo.

The consistency of the Boltzmann equation is at the heart of Lanford's Theorem. Specifically, there are two possible ways to approach the evaluation of the Boltzmann equation, and Lanford questioned their equivalence:

(1) Initial t. Let microstates of gas evolve according to classical mechanics. Then observe the final microstate and use this to determine the distribution function

(2) Solve Boltzmann equation for the distribution function at the initial time t, and use this to determine the terminal microstate.

(3) Models: Ehrenfest wind-tree 1912; Dog Flea 1907 ; Kac ring model 1959.

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CHRONOLOGY

1874 Maxwell, Thomson and Tait recognize that the Boltzmann equation does not really "explain" time irreversibility"

1876: Loschmidt *Umkehreinwand*

1890: Boltzmann publishes articles in Nature

1894: Culverwell objections

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Jos Uffink "The Boltzmann Equation and H-Theorem"
www.pitp.phas.ubc.ca/confs/7pines2009/readings/Uffink.pdf)

Uffink points out that there is nothing in the original H-Theorem that guarantees that the gas will eventually reach its stationary or minimal value. It's not certain that it shows that when it reaches this minimum it will stay there for an indefinite period.

1889 Poincaré. Classic paper: No monotonically increasing function can be defined on coordinates of a system subject to Hamiltonian dynamics

1893 Poincaré: Criticism of Boltzmann and Helmholtz arguments

1890 Zermelo *"Wiederkehreimnwand"*

1893 Poincaré: "Irreversibility is in both the premises and the conclusion"

1898: Poincaré paper on the stability of the solar system. Uses a very strange argument: *" The planets give off heat that dissipates in space, and will therefore reach a Boltzmann equilibrium."*

1896 Zermelo: The stationary limit to which Boltzmann alludes cannot be stable, and is therefore not truly stationary.

In response to Zermelo and Loschmidt, Boltzmann endorses probability.

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