

The Boltzmann Transport Equation: Theory and Applications

Matt Krens

December 10, 2007

1 Introduction

The classical theory of transport processes is based on the Boltzmann transport equation. The equation can be derived simply by defining a distribution function and inspecting its time derivative. From this equation, many important results can be derived. In addition to some of the textbook results from the Boltzmann transport equation, it is still being used in many contemporary research projects to model transport phenomena.

2 Theoretical Background

2.1 The Distribution Function

To understand the Boltzmann equation, it is important to understand the concept of a distribution function. A distribution function describes how electrons or other types of particles are distributed in real and momentum space through the course of time. For our transport problem, we want to describe a non-equilibrium distribution function since transport is an inherently non-equilibrium problem. However, we can give a familiar example of a distribution function for an equilibrium problem, the Fermi-Dirac distribution:

$$f(\mathbf{p}) = \frac{1}{e^{[E(\mathbf{p})-\mu]/kT} + 1} \quad (1)$$

where $E(\mathbf{p})$ is the energy as a function of the momentum \mathbf{p} , μ is the chemical potential, k the Boltzmann constant, and T the temperature. Here we can see how the particles are distributed as a function of momentum. We need to extend this concept to non-equilibrium problems. We can define a **phase-space density** for N interacting and indistinguishable particles by

$$D(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N, t). \quad (2)$$

This phase-space density is such that the quantity $D(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N, t)d\Omega$, where $d\Omega$ is an infinitesimal element of phase space spanned by the coordinates and momenta of all particles, is the probability that, at a time t , the particles can be found in a volume $d\Omega$ centered at $(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N)$. Since D is a probability

density, it satisfies $\int D(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N, t) d\Omega = 1$ at all times. If $d\mathbf{r}_i d\mathbf{p}_i$ is the infinitesimal phase-space volume associated with particle i , the volume $d\Omega$ is

$$d\Omega = \frac{1}{N!} \prod_{i=1}^N d\mathbf{r}_i d\mathbf{p}_i \quad (3)$$

where the factor $1/N!$ accounts for the indistinguishability of the particles. This phase-space density for all N particles is unwieldy to work with so we must figure out a simpler quantity. We can integrate out all of the phase-volume associated with all but one particle:

$$f(\mathbf{r}, \mathbf{p}, t) = \int D(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N, t) \frac{1}{(N-1)!} \prod_{i=2}^N d\mathbf{r}_i d\mathbf{p}_i \quad (4)$$

such that $f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p}$ is the number of particles at a time t found in a phase space volume $d\mathbf{r} d\mathbf{p}$ around the phase space point (\mathbf{r}, \mathbf{p}) . The total number of particles, N , is thus defined by the quantity

$$N = \int f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p} \quad (5)$$

integrated over all allowed space and momenta. We have thus defined a practical single particle non-equilibrium distribution function.

2.2 Derivation of the Boltzmann Equation

From the single particle non-equilibrium distribution function, we can derive a transport equation of motion¹. We start off by considering a set of N *non-interacting* particles subject to an external periodic potential $V_{ext}(\mathbf{r}, t)$, thus having the Hamiltonian

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + V_{ext}(\mathbf{r}_i, t). \quad (6)$$

Since we are dealing with non-interacting particles, we can use the single particle distribution function $f(\mathbf{r}, \mathbf{p}, t)$ with no approximations since the full distribution function $D(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N, t)$ factorizes into a product of N one particle distribution functions. Since the particles are governed by Hamiltonian dynamics, **Liouville's theorem** of incompressible phase space flow applies. Liouville's theorem guarantees that the phase-space volume remains constant, as well as the number of particles in a volume $d\mathbf{r} d\mathbf{p}$. This is stated mathematically as

$$\frac{df(\mathbf{r}, \mathbf{p}, t)}{dt} \equiv \frac{\partial f}{\partial t} + \sum_{i=1}^d \left(\frac{\partial f}{\partial r_i} \frac{\partial r_i}{\partial t} + \frac{\partial f}{\partial p_i} \frac{\partial p_i}{\partial t} \right) = 0 \quad (7)$$

where d is the number of dimensions. This is simply the total derivative of $f(\mathbf{r}, \mathbf{p}, t)$. This is equivalently written as

$$\frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial t} + \frac{d\mathbf{r}}{dt} \cdot \nabla_{\mathbf{r}} f(\mathbf{r}, \mathbf{p}, t) + \frac{d\mathbf{p}}{dt} \cdot \nabla_{\mathbf{p}} f(\mathbf{r}, \mathbf{p}, t) = 0 \quad (8)$$

¹much thanks to Massimiliano Di Ventra for sharing pages from his upcoming book "Electron Transport in Nanoscale Systems" which helped me greatly in writing about the theoretical background of the Boltzmann equation

where ∇ is the d -dimensional gradient operator with respect to space or momentum coordinates as indicated. We now recall Hamilton's equations of motion,

$$\frac{dr_i}{dt} = \frac{\partial H}{\partial p_i}; \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial r_i}, \quad (9)$$

where the index $i = 1, \dots, d$ and H is the single particle Hamiltonian, $H = \mathbf{p}^2/2m + V_{ext}(\mathbf{r}, t)$. We can thus arrive at

$$\frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} f(\mathbf{r}, \mathbf{p}, t) - \nabla_{\mathbf{r}} V_{ext}(\mathbf{r}, t) \cdot \nabla_{\mathbf{p}} f(\mathbf{r}, \mathbf{p}, t) = 0 \quad (10)$$

For non-interacting atoms in a periodic lattice, this equation would completely describe the phase-space dynamics of a system of particles [1]. In reality though, we must be able to quantify the motion associated with *interacting* particles in a real lattice. Consider a system of electrons interacting via a Coulomb interaction which is just a two-particle potential, $U(|\mathbf{r} - \mathbf{r}'|)$, which depends on the relative distance between the electrons. Even without the electron-electron interaction, the ionic lattice may also have impurities or crystal defects as well as there being intrinsic deviations from periodicity in a perfect crystal due to thermal vibrations of the ions. As it turns out, the effect due to vibrations in the ionic lattice dominates at high temperatures and impurity or defect scattering dominates in crystals at low temperatures. Electron-electron scattering due to the Coulomb interaction actually plays a relatively minor role in a lot of systems. Nonetheless, the presence of these interactions changes particle momenta via scattering processes such that the particles can scatter in and out of the phase space volume $d\mathbf{r}d\mathbf{p}$. The distribution function $f(\mathbf{r}, \mathbf{p}, t)$ is no longer a conserved quantity and the condition $df/dt = 0$ no longer applies. We can account for the scattering in and out of phase space volume by balancing the time rate of change of the distribution function with a time rate of change associated with the collisions. This can be expressed mathematically as

$$\frac{d}{dt} f(\mathbf{r}, \mathbf{p}, t) = \left(\frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial t} \right)_{collisions} \equiv \mathbf{I}[f] \quad (11)$$

where $\mathbf{I}[f]$ is defined to be the **collision integral** and is a functional of the distribution function. We can now arrive at the final form of the Boltzmann transport equation

$$\frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} f(\mathbf{r}, \mathbf{p}, t) - \nabla_{\mathbf{r}} V_{ext}(\mathbf{r}, t) \cdot \nabla_{\mathbf{p}} f(\mathbf{r}, \mathbf{p}, t) = \mathbf{I}[f]. \quad (12)$$

2.3 The Collision Integral

Our main problem now is to come up with a suitable form of the collision integral. For a given interaction potential, one can calculate the collision integral exactly, but in practice these are not very useful for practical applications. For example, for a two-body potential one finds the collision integral depends on a two-particle distribution function, f_2 (this time integrate the full distribution function over all but two particles). However, the equation of motion for f_2 depends on the three-particle distribution function, f_3 . Likewise, f_3 depends on f_4 , and so on. This infinite hierarchy of coupled equations is known as the

BBGKY Hierarchy. One needs to come up with a more suitable way to describe the collision integral, hopefully only involving the single particle distribution function.

We need to find an expression for the probability per unit time that an electron with momentum \mathbf{p} will suffer some collision. This quantity is $1/\tau(\mathbf{p})$ which is simply one over the time it takes between collisions as a function of momentum known as the **relaxation time**. This probability per unit time is defined in terms of a quantity $W_{\mathbf{p},\mathbf{p}'}$ where $W_{\mathbf{p},\mathbf{p}'}dt d\mathbf{p}'$ is the probability in an infinitesimal time interval dt that an electron with momentum \mathbf{p} is scattered into any one of the group of levels contained in the infinitesimal p -space volume element $d\mathbf{p}'$ about \mathbf{p}' , assuming these levels are all unoccupied and not forbidden by the exclusion principle. The particular form of $W_{\mathbf{p},\mathbf{p}'}$ depends on the particular scattering mechanism being described. Given this definition of $W_{\mathbf{p},\mathbf{p}'}$, the actual rate of transition must be reduced by the fraction of these levels that are actually unoccupied since transitions into unoccupied levels are forbidden by the exclusion principle. This fraction is simply $1 - f(\mathbf{r}, \mathbf{p}', t)$. The total probability is then given by summing over all final momentums \mathbf{p}' :

$$\frac{1}{\tau(\mathbf{p})} = \int d\mathbf{p}' W_{\mathbf{p},\mathbf{p}'} [1 - f(\mathbf{r}, \mathbf{p}', t)]. \quad (13)$$

We need to now figure out how the distribution function changes in time due to the collisions out of the infinitesimal element $d\mathbf{p}$. Note that because $dt/\tau(\mathbf{p})$ is the probability that any electron in the neighborhood of \mathbf{p} is scattered in the time interval dt , the total number of electrons per unit volume in $d\mathbf{p}$ about \mathbf{p} that suffer a collision is just $dt/\tau(\mathbf{p})$ times the number of electrons per unit volume in $d\mathbf{p}$ about \mathbf{p} , $f(\mathbf{r}, \mathbf{p}, t)d\mathbf{p}$. Thus we find the that contribution to the collision integral by particles scattering out of $d\mathbf{p}$ in the neighborhood of \mathbf{p} is

$$\mathbf{I}[f]_{out} = -\frac{f(\mathbf{r}, \mathbf{p}, t)}{\tau(\mathbf{p})}. \quad (14)$$

Since electrons can be scatter either into or out of $d\mathbf{p}$ by collisions, the collision integral $\mathbf{I}[f]$ contains the sum of two terms representing this scattering in and out of the infinitesimal momentum element $d\mathbf{p}$. We write

$$\mathbf{I}[f] = - \int d\mathbf{p}' \{W_{\mathbf{p},\mathbf{p}'} f(\mathbf{r}, \mathbf{p}, t) [1 - f(\mathbf{r}, \mathbf{p}', t)] - W_{\mathbf{p}',\mathbf{p}} f(\mathbf{r}, \mathbf{p}', t) [1 - f(\mathbf{r}, \mathbf{p}, t)]\} \quad (15)$$

where the contribution from $\mathbf{I}[f]_{in}$ is included and has the same structure as $\mathbf{I}[f]_{out}$ except for the interchange of \mathbf{p} and \mathbf{p}' . I have defined a general form for the collision integral, but this can still be unwieldy to work with so we can make a further approximation called the **relaxation-time approximation** to rewrite the collision integral as

$$\mathbf{I}[f] = -\frac{[f(\mathbf{r}, \mathbf{p}, t) - f^{eq}(\mathbf{r}, \mathbf{p})]}{\tau(\mathbf{p})} \quad (16)$$

where $f^{eq}(\mathbf{r}, \mathbf{p})$ is the local equilibrium distribution function and $\tau(\mathbf{p})$ here is a specified function of \mathbf{p} and does not depend on the distribution function. The Boltzmann transport equation can now be written as

$$\frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial \mathbf{r}} + \mathbf{F}_{ext}(\mathbf{r}, t) \cdot \frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial \mathbf{p}} = -\frac{[f(\mathbf{r}, \mathbf{p}, t) - f^{eq}(\mathbf{r}, \mathbf{p})]}{\tau(\mathbf{p})} \quad (17)$$

where I have redefined

$$\nabla_{\mathbf{r}} \equiv \frac{\partial}{\partial \mathbf{r}}, \quad \nabla_{\mathbf{p}} \equiv \frac{\partial}{\partial \mathbf{p}}, \quad -\nabla_{\mathbf{r}} V_{ext}(\mathbf{r}, t) \equiv \mathbf{F}_{ext}(\mathbf{r}, t).$$

This approximation assumes that the rate at which f returns to the equilibrium distribution, f^{eq} is proportional to the deviation of f from f^{eq} . The primary assumption behind this is that scattering merely serves to drive a non-equilibrium distribution back towards thermal equilibrium. We can see this by considering the following case. Starting in a system far from equilibrium, let us assume that the distribution f and external potential do not have large spatial variations. If this is the case, the collision integral $\mathbf{I}[f]$ dominates the dynamics as one can see from the form of the Boltzmann equation. Thus, during this transient time, the Boltzmann equation is approximately

$$\frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial t} \approx \mathbf{I}[f]. \quad (18)$$

Employing the relaxation-time approximation to the collision integral, we arrive at

$$\frac{\partial f(\mathbf{r}, \mathbf{p}, t)}{\partial t} \approx -\frac{[f(\mathbf{r}, \mathbf{p}, t) - f^{eq}(\mathbf{r}, \mathbf{p})]}{\tau} \quad (19)$$

which has the solution

$$f(\mathbf{r}, \mathbf{p}, t) = f^{eq}(\mathbf{r}, \mathbf{p}) + [f(\mathbf{r}, \mathbf{p}, t=0) - f^{eq}(\mathbf{r}, \mathbf{p})] e^{-t/\tau}. \quad (20)$$

From this, we can see that the system approaches local equilibrium in a time on the order of the relaxation time (hence the name). After this initial transient state, the other terms in the Boltzmann equation become comparable to the collision integral.

Once we find a suitable expression for the distribution function, we can calculate the **electron density**,

$$n(\mathbf{r}, t) = \int d\mathbf{p} f(\mathbf{r}, \mathbf{p}, t) \quad (21)$$

and the **current density**,

$$\mathbf{j}(\mathbf{r}, t) = \int d\mathbf{p} \frac{\mathbf{p}}{m} e f(\mathbf{r}, \mathbf{p}, t), \quad (22)$$

where e is the elementary charge. These are two very important quantities in the study of transport phenomena.

3 The Boltzmann Equation in Practice

Many classical results can be derived or supported by the Boltzmann equation. Some simple examples will be presented in the following sections. However, even contemporary researchers still sometimes employ the Boltzmann equation when trying to understand transport properties in more complex systems.

3.1 1D Particle Diffusion

We can think about using the Boltzmann equation for some very simple calculations. For the sake of simplicity, we consider an equilibrium function which only has dependence on the x-direction, i.e. $f(\mathbf{r}, \mathbf{p}, t) \rightarrow f(x, p_x, t)$. We can write the collision integral as

$$\left(\frac{\partial f(x, p_x, t)}{\partial t} \right)_{\text{collisions}} = \frac{\partial f(x, p_x, t)}{\partial x} \frac{\partial x}{\partial t} = \frac{p_x}{m} \left(\frac{\partial f}{\partial x} \right) \quad (23)$$

to arrive at

$$\frac{p_x}{m} \left(\frac{\partial f(x, p_x, t)}{\partial x} \right) = - \frac{[f(x, p_x, t) - f^{eq}(x, p_x)]}{\tau} \quad (24)$$

with the relaxation time approximation employed. Then we can say that to first order,

$$f_1(x, p_x) \simeq f^{eq}(x, p_x) - \frac{p_x}{m} \tau \left(\frac{\partial f^{eq}(x, p_x)}{\partial x} \right) \quad (25)$$

with $\partial f(x, p_x, t)/\partial x$ replaced with $\partial f^{eq}(x, p_x)/\partial x$. The equilibrium distribution function can be a variety of things, but often the classical distribution

$$f^{eq}(x, p_x) = e^{(\mu(x) - E(p_x))/kT}, \quad (26)$$

or, in the case of electrons, the Fermi-Dirac distribution

$$f^{eq}(x, p_x) = \frac{1}{e^{[E(p_x) - \mu(x)]/kT} + 1} \quad (27)$$

is employed. See Appendix F of [2] for simple calculations involving the 1D Boltzmann equation and diffusion.

3.2 Electrical Conductivity

If one assumes the external potential is that of an electric field, then with a Fermi-Dirac distribution at constant T employing the relaxation time approximation, Eq.[17] becomes

$$\left(\frac{\partial f^{eq}}{\partial \mathcal{E}} \right) \frac{\mathbf{p}}{m} \cdot e\mathbf{E} = - \frac{[f - f^{eq}]}{\tau} \quad (28)$$

where \mathcal{E} is the energy, e is the charge, and we have used $\frac{\mathbf{p}}{m} = \frac{\partial \mathcal{E}}{\partial \mathbf{p}}$ to transform one of the derivatives. We have also assumed that the distribution function, f , does not depend explicitly on the time, t . Now we can write the distribution function f as

$$f = \tau f^{eq} - \frac{\mathbf{p}}{m} \cdot e\tau \mathbf{E} \left(\frac{\partial f^{eq}}{\partial \mathcal{E}} \right). \quad (29)$$

Now we can use the expression for the current density, Eq.[22], to write

$$\mathbf{J} = \int d\mathbf{p} \frac{\mathbf{p}}{m} e \left[\tau f^{eq} - \frac{\mathbf{p}}{m} \cdot e\tau \mathbf{E} \left(\frac{\partial f^{eq}}{\partial \mathcal{E}} \right) \right]. \quad (30)$$

There is no current density associated with the equilibrium distribution function, f^{eq} , obviously, and we can write the current density as

$$\mathbf{J} = \frac{1}{4\pi^3 \hbar m} \int \int e^2 \tau \mathbf{p} (\mathbf{p} \cdot \mathbf{E}) \left(- \frac{\partial f^{eq}}{\partial \mathcal{E}} \right) \frac{dS}{p} d\mathcal{E} \quad (31)$$

where we have transformed the integral over the momentum space volume to one over surfaces of constant energy. For the details, please see [5]. We can further say that, at least for a metal, the function $(-\partial f^{eq}/\partial \mathcal{E})$ behaves like a delta function at the Fermi level, so we are left with an integral over the Fermi surface

$$\mathbf{J} = \frac{1}{4\pi^3} \frac{e^2 \tau}{\hbar m} \int \frac{\mathbf{p} \mathbf{p} dS_f}{p} \cdot \mathbf{E}. \quad (32)$$

We can compare this with the macroscopic form of **Ohm's Law**

$$\mathbf{J} = \sigma \cdot \mathbf{E} \quad (33)$$

and identify the **conductivity tensor** in dyadic notation as

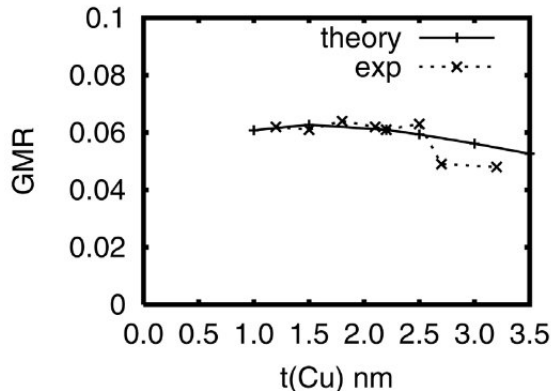
$$\sigma = \frac{1}{4\pi^3} \frac{e^2 \tau}{\hbar m} \int \frac{\mathbf{p} \mathbf{p} dS_f}{p}. \quad (34)$$

This is an example of one of the classical results one can obtain from the Boltzmann equation. It can be compared with results derived from other theories such as the Kubo formalism. Additionally by adding in a magnetic field, one can derive the **Hall effect** from the Boltzmann transport equation. See [5] for the details of this.

3.3 Boltzmann Transport for Spin Valves

In the previous section, I presented a textbook example of what you can calculate with the Boltzmann transport equation. However, even today, this century old equation is finding applications in modern research. In a 2000 paper by Maclaren et al. [3] called “First Principles Based Solution to the Boltzmann Transport Equation for Co/Cu/Co Spin Valves” the authors study transport in layered magnetic materials. The approach they employ is used to study the variation in **giant magnetoresistance** (GMR) with individual layer thickness.

The particular application of the Boltzmann equation used in this paper is to study transport in spin valves. A **spin valve** is a device consisting of two or more conducting magnetic materials, that alternates its electrical resistance depending on the alignment of the magnetic layers, in order to exploit the giant magnetoresistance effect. A spin valve consists of two magnetic layers separated by a spacer layer chosen to ensure that the coupling between magnetic layers is weak. The magnetic orientation of one layer is also “pinned” in one direction by adding a fourth layer: a strong antiferromagnet. When a weak magnetic field, such as that from a bit on a hard disk, passes beneath such a structure, the magnetic orientation of the unpinned magnetic layer rotates relative to that of the pinned layer, generating a significant change in electrical resistance due to the GMR effect. Spin valve GMR is, in fact, the most useful form of GMR and is used in essentially all hard disk drives.



Solving the Boltzmann transport equation is one part in the step of understanding how GMR varies with layer thickness. The details can be found in [3, 4]. The Boltzmann transport equation is used within each distinct layer to study CIP (Current In the Plane) and CPP (Current Perpendicular to the Plane) transport for the spin valves. It is hard to predict the accuracy of the Boltzmann equation in this problem because many additional theoretical techniques and procedures have gone into producing the results. Nonetheless, the paper presented the variation of GMR with Cu layer thickness. As one can see in the graph, there is good agreement up until about 2.5 nm.

4 Conclusion

The Boltzmann transport equation can be derived by considering how a distribution function changes in time. There are various approximations and phenomenological approaches which make the equation useful and solvable for simple systems. The equation can describe macroscopic phenomena such as the electrical conductivity, Hall effect, and diffusion process. It has proved fruitful not only for the study of the classical gases Boltzmann had in mind, but also, properly generalized, for other systems such as electron transport, photon transport in superfluids, and radiative transport in planetary and stellar atmospheres. It still has much relevance to modern transport theory. While the Boltzmann transport equation is more of a macroscopic, statistical approach to transport, especially relevant to diffusion processes, modern transport techniques such as **time-dependent density functional theory** (TDDFT) capture more of the microscopic picture including the quantum nature of the problem. Despite its limitations, the Boltzmann equation still has much use and applicability.

References

- [1] Neil W. Ashcroft and N. David Mermin. *Solid State Physics*. Thomson Learning, 1st edition, 1976.
- [2] Charles Kittel. *Introduction to Solid State Physics*. Wiley, 7th edition, 1996.
- [3] J.M. MacLaren, L. Malkinski, and J.Q. Wang. First principles based solution to the boltzmann transport equation for co/cu/co spin valves. *Material Research Society*, 2000.
- [4] J.M. MacLaren, X.-G. Zhang, W.H. Butler, and Xindong Wang. Layer kkr approach to bloch-wave transmission and reflection: Application to spin-dependent tunneling. *Phys. Rev. B*, 59(8):5470–5478, 1999.
- [5] J.M. Ziman. *Principles of the Theory of Solids*. Cambridge, 2nd edition, 1972.