

Experimental Validation of the Unified Theory

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Abstract

Hatsopoulos and Gyftopoulos (1976a,b,c,d) founded the Unified Quantum Theory of Mechanics and Thermodynamics. This theory encompasses both quantum mechanics and thermodynamics within a single mathematical framework. Unlike statistical approaches, it treats thermodynamics as a non-statistical (hence, a physical) theory and is intended to describe all reversible and irreversible phenomena. Unfortunately, the theory has long been criticized for not bringing anything new beyond statistical quantum thermodynamics. To break through this misconception that thermodynamics is a statistical theory, experimental validation at a microscopic scale, where statistical effects are negligible, would be fruitful. In this paper, which is based on the dissertation work of the author (1993), experiments that were previously reported are investigated within the framework of the new theory. It is argued that they provide an undeniable confirmation of the theory and the existence of irreversibility at the microscopic scale.

Keywords: Gyftopoulos-Hatsopoulos unified quantum theory of mechanics and thermodynamics, non-statistical (physical) theory of thermodynamics, equation of motion for reversible and irreversible processes, dynamical law, microscopic irreversibility, experimental validation

1. Introduction

This paper which is based on the dissertation work of the author (1993) is intended to provide an experimental validation of the Unified Quantum Theory of Mechanics and Thermodynamics founded by Hatsopoulos and Gyftopoulos (1976a,b,c,d). This theory encompasses both quantum mechanics and thermodynamics within a single mathematical framework.

Because its dynamical law implies a so-called unitary time evolution, quantum mechanics cannot describe irreversible phenomena (Wehrl, 1978). To be more specific, it can only describe some of the reversible phenomena. An important novelty introduced by the Unified Theory to the quantum physics, is that its dynamical law (Beretta et al., 1984; Beretta, Gyftopoulos, and Park, 1985) incorporates both irreversible and all reversible (whether unitary or not) physical phenomena.

The Unified Theory, like all other physical theories, is developed to conform to our

observations of physical phenomena. Therefore, numerous experimental validations of the theory were available, even at the earliest stages of the development of the theory. Because quantum mechanics is, for instance, a special case of the theory, any experimental validation of quantum mechanics is in turn a confirmation of the Unified Theory as well.

To appreciate the novelties brought by the new theory, however, we need to demonstrate the existence of a set of physical phenomena, which is contemplated by the Unified Theory and not by quantum mechanics. To this end, irreversible processes represent an important candidate. The majority of the experiments, in which irreversible time evolutions are observed, are performed on systems containing a large number of constituents (molecules or particles). Such systems are referred to as macroscopic systems in the literature.

Many efforts have been made to describe these observed irreversibilities at the macroscopic level. In such approaches, statistical mechanics is used in conjunction with quantum mecha-

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tics; hence the theory of statistical quantum mechanics was developed. In statistical quantum mechanics, the challenge was to describe macroscopic irreversibility in terms of microscopic reversibility. All these efforts ended up in inconsistencies, however, and no satisfactory explanation to the question of irreversibility has been found in statistical quantum mechanics. Among such inconsistencies is the alteration of the dynamical law of the theory, which is the von Neumann Equation, to produce phenomenological time evolution equations.

The Unified Theory brought a new breath to physics, by stating that irreversibility does not occur at the macroscopic level as suggested by statistical quantum mechanics but rather is inherent to the nature of the system. In the jargon of statistical quantum mechanics, irreversibility occurs at the microscopic level. This approach is deprived of the inconsistencies present in statistical quantum mechanics.

To validate the assertion that irreversibility is actually a direct implication of the dynamical law of physics, an experiment must be devised with a small number of molecules or particles such that the observed irreversibility cannot be attributed to statistics. To this end, the study of the free precession of spins, through the use of an optical pumping technique, provides an ideal example

2. Unified Quantum Theory of Mechanics and Thermodynamics

As its name suggests, the new theory is a generalization of quantum mechanics designed to encompass within a single physical theory all the results of quantum mechanics and thermodynamics. Even though the mathematical structure of the theory resembles to that of statistical quantum mechanics, it is a non-statistical theory. A brief description of its mathematical structure is summarized below.

2.1 States

The first step in the generalization of quantum mechanics is achieved by accepting the existence of not previously conceived of states of systems. In conventional quantum mechanics, states are represented by an element of a separable Hilbert space. In many textbooks on quantum mechanics, the chosen Hilbert space is the space of square integrable functions in which case the state is referred to as the wave function.

An alternative mathematical structure for quantum mechanics has also been developed, in which states are represented by projection operators, ρ , on the Hilbert space. Formally, these operators are linear, self-adjoint, non-negative definite, unit-trace operators on the

separable Hilbert space, which are idempotent, i.e., $\rho^2 = \rho$.

Using the latter mathematical framework, in the Unified Theory, it is postulated that states are represented by linear, self-adjoint, non-negative definite, unit trace operators on a separable Hilbert space. However, the requirement that the operator is idempotent (equivalently, is a projection operator) is relaxed. That is, the existence of operators with $\rho^2 \neq \rho$ is accepted, in addition to operators satisfying the relation $\rho^2 = \rho$.

In rigorous treatments of quantum mechanics, the need for broadening the set of state operators to include non-idempotent ones became apparent (Park 1968a,b,c; Park, 1988; Jauch, 1968). However, their existences were not postulated firmly until the foundations of the Unified Theory by Hatsopoulos and Gyftopoulos (1976a,b,c,d).

To envisage and appreciate the non-statistical aspect of the Unified Theory, it is important to scrutinize the similarity between the state operator of the theory and the statistical operator presented in statistical quantum mechanics. Even though, state operators and statistical operators are identical mathematical objects, they correspond to entirely different physical concepts. The state operator in the Unified Theory refers to an individual state of a system, i.e., is attributed to a strictly homogeneous ensemble. Whereas, the statistical operator of statistical quantum mechanics corresponds to a heterogeneous ensemble and is intended to describe the statistical mixing of quantum mechanical states. An excellent treatment of the concepts of homogeneous and heterogeneous ensembles is presented by von Neumann (1955).

2.2 Properties

The next step in the generalization procedure of quantum mechanics involves the properties attributed to systems. Because the Unified Theory encompasses mechanics as a special case, all the properties defined and studied within the framework of quantum mechanics do also exist in the new theory. In quantum mechanics, to every physical property, there corresponds a linear, self-adjoint, closed operator. However, it is important to note that the converse statement is not correct, namely, that there exist linear, self-adjoint, closed operators that do not correspond to any physical observable (Wick, Wightman, and Wigner, 1952).

As expected from the generalization procedure, a set of properties may be added to the ones contemplated by quantum mechanics.

This is indeed the case and in the Unified Quantum Theory of Mechanics and Thermodynamics, the existence of properties, which do not correspond to a linear, self-adjoint, closed operator is postulated. Entropy is an example of such a property, as its value is expressed in terms of a non-linear functional of the state operator (Gyftopoulos and Çubukçu, 1997).

This last statement emphasizes the non-statistical characteristics of the Unified Theory, in which entropy is accepted as a property of the system and a definite value for it is assigned at every state of any system. This way of understanding and modeling physical phenomena reflects a perfect match with how the principles and implications of general thermodynamics are stated without ambiguities, inconsistencies, and circular arguments (Gyftopoulos and Beretta, 1991).

In statistical quantum mechanics, on the other hand, entropy does not represent an inherent property of the system but rather reflects the measure of the amount of information that an observer has about the state of the system. This notion of entropy has nothing to do with the concept of entropy presented either in the Unified Theory or in general thermodynamics.

2.3 Dynamical law

The description of the time evolution of the states of a physical system, namely, the dynamical law constitutes the next postulate of the Unified Theory. Again, as quantum mechanics is a special case of the theory, the time evolution of the states represented by idempotent state operators (satisfying $\rho^2=\rho$) obey the Schrödinger equation or equivalently the von Neumann equation. However, the time evolution of non-mechanical states (with $\rho^2\neq\rho$) remained to be postulated at the foundations of the theory (Gyftopoulos and Hatsopoulos, 1976a,b,c,d).

Jauch (1968) who is also aware of the existence of states to which a non-idempotent state operator must be assigned, further postulated that the von Neumann equation is valid for all states. This postulate, which has no inconsistency, fails to comply, however, with our observation of physical phenomena. It is straightforward to demonstrate that this dynamical law implies a unitary time evolution (Messiah, 1961; Jancel, 1969) and, thus, excludes the possibility of an irreversible adiabatic change of state. However, the power of a physical theory lies in its ability to make predictions and, therefore, its dynamical law must be able to describe all reversible and irreversible phenomena. Hence, the dynamical law of the Unified Theory cannot be the von Neumann equation for all states.

Important developments have been made in identifying the equation of motion of the Unified Theory (Beretta et al., 1884; Beretta, Gyftopoulos, and Park, 1985). At this stage, it is compulsory to underline the fact that the dynamical law of any physical theory should be discovered and not derived. Throughout the development of the science of physics, this has been achieved by postulating the dynamical law and then assessing its validity by comparing its predictions with our observations of actual physical phenomena. Newton's law of time evolution, for instance, was a postulate and it turned out to be very successful, until the observations leading to the foundations of the theory of special relativity were made.

Our knowledge of physical phenomena and the mathematical framework of the Unified Theory impose severe restrictions on the structure of the equation of motion. Çubukçu and Gyftopoulos (1995) stated a set of criteria that must be satisfied by the dynamical law of the theory. They further investigated whether the proposed modifications to either the von Neumann or the Schrödinger equation available in the literature comply with this set of restrictions. They concluded that among all candidates, only the equation suggested by Beretta has an acceptable mathematical structure (Beretta et al., 1984; Beretta, Gyftopoulos, and Park, 1985).

The equation postulated by Beretta is a generalization of the von Neumann equation, rather than a modification. For all mechanical states (i.e., states represented by idempotent state operators), the Beretta equation reduces precisely to the von Neumann equation. For non-mechanical states, i.e. states represented by a non-idempotent state operator, on the other hand, a non-unitary evolution is in general implied. Therefore, by adopting Beretta's equation as the dynamical postulate of the Unified Theory, quantum mechanics becomes an exact special case of the newly developed theory. With this view in mind, Hatsopoulos and Gyftopoulos (1976a,b,c,d) emphasized that the von Neumann equation is incomplete, namely, that it is valid for only a limited class of states, and its generalization, which can be applied to any physical state, remains to be discovered.

3. Predictions of the Theory

Because quantum mechanics is an exact special case of The Unified Quantum Theory of Mechanics and Thermodynamics, all the justifications of the former are valid for the latter. The power of and the novelty brought by the Unified Theory can then be appreciated by its description of non-unitary time evolutions.

Among non-unitary phenomena, irreversible adiabatic changes of states attract the most attention.

Beretta and co-workers (Beretta et al., 1984; Beretta, Gyftopoulos, and Park, 1985) have demonstrated that the proposed equation of motion takes the majority of states (states represented by an operator with all non-negative eigenvalues) to the corresponding thermodynamic equilibrium state with the same value of energy. In this way, the Unified Theory simulates the internal rate of entropy generation in an isolated system.

3.1 Observation of the irreversibility at the macroscopic scale

Many entropy increasing, adiabatic changes of states in isolated systems are familiar both to physicists and to engineers. A relatively simple example is the mixing of hot and cold water in a well-insulated container to produce lukewarm water.

Internal discharge of a perfectly insulated electric battery is another example. As time passes by, we observe a physical change in the state of the battery: the output voltage has decreased and when touched, we feel that the battery is warmer than its original state. It is well-known that the amount of work that can be extracted from the battery has also been reduced (in the language of thermodynamics, its entropy has increased, while its energy remained invariant, because it was isolated).

From an information theoretic point of view, in the above described irreversible adiabatic changes of states, the time evolutions are perfectly reversible and the increase in entropy is a result of the growing obsolescence of our past knowledge about the state of the system. Therefore, the increase in entropy is in the mind of the observer and does not represent an objective dynamical process. This approach undeniably disagrees with our observation. Our observation that the water is lukewarm or that the battery is warm and incapable of supplying electric power is physical, objective (i.e. independent of the observer) and can be verified by repeated measurements.

3.2 An analogy from quantum mechanics

No matter whether the information theoretic or the phenomenological approach is taken, irreversibility in statistical quantum mechanics has not yet been successfully explained. Within the framework of statistical quantum mechanics, irreversibility is considered to occur only at the macroscopic level, whereas at the microscopic level phenomena are reversible. Introducing the Boltzmann equation in addition to the von

Neumann equation or adding postulates to those of thermodynamics (De Groot and Mazur, 1962) are among the efforts made to establish the relationship between macroscopic irreversibility and microscopic reversibility.

In many of these discussions, collisions among gas molecules are considered. This is essential in expressing the Boltzmann equation. The concept of collision arises from the kinetic theory of gases in which gas molecules are considered to be point particles that move back and forth in a container. The kinetic theory of gases is developed as a statistical classical theory. With the development of quantum mechanics, work has been done to derive the kinetic theory of gases as a statistical quantum mechanical theory. This treatment results in the so-called grand-canonical distribution for the statistical operator, when the gas is in thermodynamic equilibrium. It is a well-known feature of canonical distributions that they are diagonal in energy representation, i.e. commute with the Hamiltonian. It immediately follows that the expectation value of the momentum for each gas molecule is zero. This result is rather surprising, since quite contrary to the statistical classical treatment of the kinetic theory of gases where the gas molecules are flying back and forth in the container, quantum theory predicts that they are not moving at all. Therefore, in thermodynamic equilibrium, there can be no collisions among the gas molecules, at least in the formalism of the Boltzmann equation.

The rather surprising and striking conclusion that in thermodynamic equilibrium gas molecules are at rest is greatly overlooked and even ignored in statistical mechanics. Many rigorous treatments derive the grand-canonical distribution but then make use of the classical theory instead of using the quantal description, since use of the Boltzmann equation involving collisions is needed to proceed further. Such an approach, however, i.e., invoking the Boltzmann equation into statistical quantum mechanics, leads to an inconsistency within the theory itself.

Before providing further evidence that in thermodynamic equilibrium gas molecules are stationary, it is essential to review the treatment of the kinetic theory of gases within the framework of the Unified Theory. This straightforward process leads to the grand-canonical distribution of the state operator (as expected, because the mathematical structure of the theory resembles that of statistical quantum mechanics). It follows that the expectation value of the momentum of each gas molecule is zero, hence the gas molecules are not moving. This conforms to our observation that the system is in a thermodynamic equilibrium (stable

equilibrium) state where the notion of equilibrium itself suggests that nothing is in motion (changes with time). Even though the gas molecules are at rest, they occupy the entire volume of the container and their distribution is fairly smooth, as shown by Gyftopoulos and von Spakovsky (2001).

When teaching quantum mechanics, the following prediction of the theory is widely presented in order to demonstrate its power and novelty over the classical theories: An electron orbiting the proton does not radiate, hence a stable hydrogen atom can form. In the classical theory however, the electron orbiting the proton is subject to acceleration and since it is electrically charged should radiate according to the electromagnetic theory. This radiation implies a loss in the kinetic energy of the electron, causing the hydrogen atom to be unstable.

The novelty brought by quantum mechanics in this example, is that the electron is not accelerating. Electromagnetic theory remains valid, yet the lack of acceleration leads to the no net radiation and thus the prediction of the stability of the hydrogen atom.

An analogous conclusion within the framework of the Unified Theory directly follows: An ionized gas confined in an isolated container can remain in a thermodynamic equilibrium (i.e. stable equilibrium) state, without radiating. If the statistical classical approach were correct, the gas molecules would be flying freely inside the container and, therefore, be subject to acceleration when bouncing back from the walls of the container. The same holds true, when efforts are made to introduce the Boltzmann Equation within the framework of statistical quantum mechanics. This acceleration would cause the gas molecules to radiate, the electromagnetic theory remaining valid (this is the reason why the ionized gas is given as an example). However, they do not, and, hence, they are not moving in the same way that the electron is not moving with respect to the proton in a hydrogen atom in thermodynamic equilibrium.

4. Experimental Validation

The Unified Theory, in which entropy is taken to be a property of the system defined at all states, describes irreversible phenomena as a direct result of its dynamical law. No additional arguments, which in turn destroy the self-consistency of the theory, have to be introduced as in the case of statistical quantum mechanics. Therefore, as opposed to statistical quantum mechanics, irreversibility is considered to occur at the microscopic level (according to the new

theory, there is no microscopic or macroscopic level; these are the jargons of statistical quantum mechanics).

The Unified Quantum Theory of Mechanics and Thermodynamics successfully describes all the above mentioned phenomena. However, as mentioned above, it has long been criticized as not bringing anything new beyond the statistical treatment of quantum mechanics. The discussion about the mixing of hot and cold water, the internal discharge of the electric battery, or the motionless existence of the gas molecules in thermodynamic equilibrium are distinct features of the theory not covered by either quantum mechanics or its statistical treatment.

Generalization of a physical theory, however, is a rather painful process for its founders. Convincing a general audience as to the incompleteness of a physical theory (as happened in the case of quantum mechanics) requires great efforts. This is partially due to the reluctance of the human being to change what he/she has already learned.

The resistance that needs to be overcome has concentrated on the experimental validation of the new theory where statistical effects are negligible. These experiments have been able to demonstrate the undeniable need for the generalization of quantum mechanics deprived of (the support of!) statistics.

The power of any physical theory lies in its ability to make predictions. Hence, an experiment demonstrating the validity of its dynamical law is essential.

4.1 The case of quantum mechanics

Before attacking the problem of demonstrating the validity of the Unified Theory by devising an experiment in which so few particles are involved that the ambiguity introduced by statistics is negligible, let us pause for a moment and review how quantum mechanics has been validated.

The majority of the success of quantum theory lies in its kinematics part: Discrete structure of the energy levels of the hydrogen atom, the spin behavior of the electrons and the atoms, the discrete behavior of the specific heat, etc.

The dynamical aspect of the theory has been validated, for instance, by the stability of the hydrogen atom, as described previously. The same line of thought leads us to the validity of the Unified Theory in studying the kinetic theory of gases.

When teaching and presenting quantum mechanics, a great deal of importance is attributed to the time-dependent solutions of its

dynamical law, the Schrödinger equation (hence, the von Neumann equation). It is both surprising and striking, however, that there are very few experiments presented in the textbooks that assess the validity of these predictions. In contrast, Newton's equation in classical mechanics, which is the counterpart of Schrödinger's equation, is verified by innumerable experiments such as the study of the trajectory of a projectile in a gravity field.

In many textbooks, no experimental validation of the Schrödinger equation, other than its reduction to the Newton equation through the "Ehrenfest correspondence principle" is presented. If the only justification of the dynamical law of quantum mechanics were its reduction down to the dynamical law of classical mechanics, there would be no need of employing the new theory.

Noting that lack of experimental validation of the dynamical law of quantum mechanics, Kukolich (1968) performed a nice experiment for college students. In this experiment, the free precession of the spin states of rubidium atoms (in the vapor phase) in a magnetic field is observed. Optical pumping is used to prepare the spin state orientated in a definite direction. The magnetic field is then quickly switched from its original direction to a direction perpendicular to it. The pumping light transmitted through the rubidium vapor is used as a probe to identify the instantaneous spin state of the rubidium atoms.

The partial pressures of the rubidium vapor and the filling krypton gas are extremely small in the experiment. The system is therefore so dilute as to allow tracking the time-dependent spin behavior of individual atoms.

The time-dependent solution of the Schrödinger equation predicts a perfect oscillatory behavior in the absorption rate of the transmitted light. The experimental result exhibits the oscillatory behavior, as shown in *Figure 1* (presented in its original form given by Kukolich), thus, confirming the validity of the dynamical law of quantum mechanics.

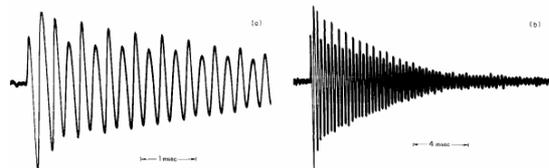


Figure 1. Experimental photocell current as a function of time after the field is switched to the x direction. Frequency of the $2\omega_p$ component is 4 kHz (Kukolich, 1968).

4.2 The case of the Unified Theory

To provide undeniable evidence of the validity of the Unified Theory, experiments that demonstrate the existence of the irreversibility at the microscopic level would be fruitful. To this end, one needs to devise experiments in which so few particles are involved that statistical effects can be ruled out.

Beretta (1985a) proposed to study resonance fluorescence to assert the validity of his equation, which is the dynamical law of the Unified Theory. The predictions of the new theory deviate from the predictions of (statistical) quantum mechanics. Hence, once performed, this experiment would provide an undeniable validation of the new theory.

The experiment proposed by Beretta has not been performed to date. However, in the meantime, further analyses of already performed experiments can be made and searched for clues of the deviation of the prediction of the Unified Theory from that of quantum mechanics. This also has the advantage of ruling out any potential argument about the bias of the experimenter.

The Kukolich experiment provides an excellent opportunity to this end. First of all, because quantum mechanics is an exact special case of the Unified Theory, it also validates the latter. Unless, further conclusions can be drawn however, there would be no need for the generalization of quantum mechanics and recall for the Unified Theory.

Even a simple examination of *Figure 1*, reveals the existence of a considerable amount of damping in addition to the oscillatory behavior in the absorption rate of the transmitted light. This damping effect does not agree with the Schrödinger equation, the dynamical law of quantum mechanics.

If we study the same experiment in the context of the Unified Theory by noting that the initial state is close but not identical to a mechanical state (i.e. represented by a non-idempotent state operator very close to the idempotent state operator considered in the study), we would expect to have the observed damping in addition to the oscillatory behavior. An approximate solution of the Beretta equation for a spin- $\frac{1}{2}$ (two-level) system is given by Beretta (1985b). In this experiment, the corresponding rubidium spin being 2, the solution of the Beretta equation for a five-level system must be evaluated for a perfect match. Regardless of the number of levels (i.e. the spin value), the Beretta equation makes better predictions than the Schrödinger equation. Hence, the experiment performed by Kukolich provides the justification of the dynamical law of

the Unified Theory rather than that of quantum mechanics.

Another similar experiment was performed by Franzen (1959) again using rubidium vapor. Several different buffer gases were employed in the experiment. Striking results, however, were obtained when there was no buffer gas in the container subjected to optical pumping. In this experiment again, the time-dependent spin relaxation of optically aligned rubidium vapor was studied.

Instead of suddenly switching the orientation of the magnetic, Franzen by the use of a mechanical shutter cuts off the pumping light. After a known interval of time, the vapor cell is again exposed to the pumping light. Because of the spin relaxation, the rubidium vapor left in the dark evolves to a new state, which can be determined from its degree of transparency to the pumping light.

Spin relaxation in the rubidium vapor left in the dark is not predicted by quantum mechanics. However, this relaxation behavior is an intrinsic characteristic of the Beretta equation, which estimates that the spin sub-system shall evolve towards the mutual thermodynamic equilibrium state with the translational sub-system of the rubidium vapor.

The importance of the Franzen experiment lies in its technique which allows the study of the time-dependent behavior of the spins of rubidium vapor through the use of a special coating material applied on the internal surface of the vapor cell, thus, eliminating the need for a buffer gas. This method of lining the inner surface of the vapor cell can also be applied in the apparatus of Kukolich to further eliminate ambiguities.

Spin relaxation in the Franzen experiment is attributed to the collisions of Rubidium vapor atoms with each other and with the walls of the cell. However, as described previously, in thermodynamic equilibrium, rubidium vapor atoms do not move and introducing collisions produces an inconsistency in the quantum theoretical treatment of the phenomenon.

Furthermore, Franzen noted that the relaxation time is almost independent of the vapor pressure of rubidium as shown in *Figure 2* (presented in its original form given by Franzen).

If the spin relaxation were due to collisions (as it should not be, because according to the quantum theoretical treatment of the kinetic theory of gases, the vapor molecules are stationary), one would expect to observe an inverse proportional relationship between the relaxation time and the rubidium vapor pressure. This is not observed and the vapor pressure's

independent spin relaxation time is, thus, nothing but a direct manifestation of the microscopic irreversibility accepted by the Unified Theory and predicted by the Beretta equation.

5. Conclusion

The spin relaxation experiment proposed by Franzen provides a firm justification for the existence of irreversibility at the microscopic level. The results of this experiment coincide with the predictions of the dynamical law of the Unified Theory.

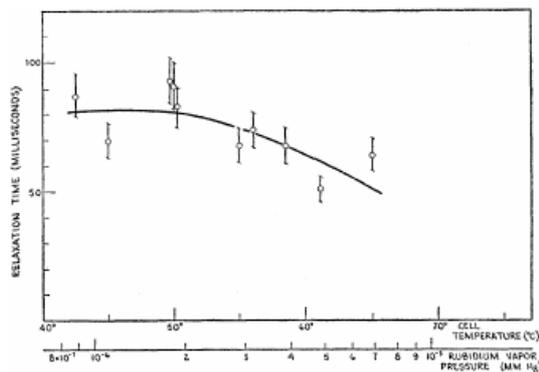


Figure 2. Variation of the relaxation time with the rubidium vapor pressure for an evacuated cell lined with tetracontane (Franzen, 1959).

The experiment performed by Kukolich, which provides a validation of the dynamical law of the Unified Theory rather than that of quantum mechanics, can be further improved by the techniques used in the Franzen experiments. Such a refined version of the experiment would reveal the detailed structure of the dynamical law of the new theory.

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