

## **A Unified Quantum Theory of Mechanics and Thermodynamics. Part III. Irreducible Quantal Dispersions<sup>1</sup>**

**George N. Hatsopoulos<sup>2</sup> and Elias P. Gyftopoulos<sup>2</sup>**

*Received June 6, 1975*

---

*This part of the paper concludes the presentation of the unified theory. It is shown that the theory requires the existence of, and applies only to, irreducible quantal dispersions associated with pure or mixed states. Two experimental procedures are given for the operational verification of such dispersions. Because the existence of irreducible dispersions associated with mixed states is required by Postulate 4 of the theory, and because Postulate 4 expresses the basic implications of the second law of classical thermodynamics, it is concluded that the second law is a manifestation of phenomena characteristic of irreducible quantal dispersions associated with the elementary constituents of matter.*

---

### **4. ON THE MEANING OF STATE**

This last part of the paper presents the precise definition of a state (pure or mixed) that is subject to the predictions of the unified theory and develops criteria for the unambiguous identification of such a state.

#### **4.1. Quantum Mechanical Considerations**

The dominant theme of quantum theory is that its causal statements about a system are probabilistic. In other words, the epistemic rule of

---

<sup>1</sup> Parts I, IIa, and IIb of this paper appeared in *Found. Phys.* **6**, 15, 127, 439 (1976), respectively. The numbering of the sections, equations, and references in this part continues from the previous parts.

<sup>2</sup> Massachusetts Institute of Technology, Cambridge, Massachusetts.

correspondence,<sup>(17)</sup> which relates experience to quantum-theoretical states, involves probabilistic concepts in an essential way. In particular, an essential premise of quantum theory is that the physical condition or state of a system at a given time cannot be fully disclosed experimentally unless many measurements are made on replicas of the system prepared in a specified manner. Conversely, an inherent prerequisite of quantum theory is that a preparation of a system be specified and uniquely associated with a state prior to any attempt to reveal experimentally the characteristics of the state. It is this prerequisite that clearly distinguishes quantum mechanics from classical mechanics. It has been discussed extensively in the literature.<sup>(18)</sup>

According to Theorem 2.5, Part I, the index of measurement statistics corresponding to a given preparation can be expressed in the form of a density operator  $\hat{\rho}$ . Some preparations result in states described by density operators that are pure, and some in states described by density operators that are mixed. In the context of the quantum mechanical Postulates 1–3, Part I, the preceding sentence is all that need be said about any given preparation and, therefore, any given state.

It is frequently stated that a mixed density operator refers to an ensemble made up of systems each of which is in a pure state. Such a statement, as pointed out by Park,<sup>(18)</sup> is meaningless. In quantum theory, the only experimentally observed reality is that which is revealed by the statistics of measurements performed on an ensemble of identical systems prepared in a specified manner. If a given preparation results in a mixed density operator, then this operator represents the only meaningful reality of the state. Park<sup>(18)</sup> points out that a general quantum ensemble characterized by a density operator  $\hat{\rho}$  can be numerically (as opposed to operationally) subdivided in an infinite variety of ways into pure or mixed subensembles, namely

$$\hat{\rho} = \sum_k w_k \hat{\rho}_k \quad \text{and} \quad \sum_k w_k = 1 \quad (50)$$

where  $\hat{\rho}_k$  is pure or mixed and  $0 < w_k < 1$  for all  $k$ .

On the other hand, we may raise a different question: Is it possible to establish an operationally meaningful criterion that will distinguish between (i) preparations resulting in dispersions that are due partially to nonquantum effects (or to lack of knowledge) and partially to quantum effects and (ii) preparations resulting in dispersions that are solely due to quantum effects? The answer to this question is yes. Prior to presenting the criterion, however, we shall show in Section 4.2 that the stable-equilibrium postulate requires an explicit operational definition of the term *identically prepared systems*.

## 4.2. On Physically Nonequivalent Density Operators

Postulate 4, Part I, reveals that the quantity  $-k \text{Tr}(\hat{\rho} \ln \hat{\rho})$  measures the fraction of the energy of a system that cannot be extracted adiabatically from the system. It thus provides the present theory with the means to account for classical thermodynamics, a branch of science that abounds in experimental information. But close examination of which types of  $\hat{\rho}$ 's are consistent with classical thermodynamics reveals an inconsistency that can be resolved only through a more refined definition of state than that used in expositions of quantum mechanics.

Postulate 4 avers the existence of stable equilibrium states. By virtue of Theorem 3.6, Part IIa, the energy of such a state cannot be reduced by means of any adiabatic CCP process. In view of the relation between preparation and state discussed in Section 4.1, we may say that Postulate 4 avers the existence of systems that have been so prepared that no energy can be extracted from them by means of any adiabatic CCP process. We shall call such a preparation *stable*. It follows from Theorem 3.23, Part IIb, that to every stable preparation there corresponds a canonical operator  $\hat{\rho}_0$  representing the measurement statistics.

But a canonical operator representing measurement statistics does not necessarily correspond to a stable preparation. That is, some such operators represent states from which work may be extracted by means of an adiabatic process, as shown by the following example.

We will consider a number  $N$  of distinctly different preparations  $Z_1, Z_2, \dots, Z_N$  having the following properties: (1) If applied to a system separately, they would result in quantum ensembles characterized by density operators  $\hat{\rho}_1, \hat{\rho}_2, \dots, \hat{\rho}_N$ ; (2) none of the operators  $\hat{\rho}_1, \hat{\rho}_2, \dots, \hat{\rho}_N$  is canonical; and (3) the sum  $(1/N) \sum_k \hat{\rho}_k$  is a canonical operator  $\hat{\rho}_0$ , namely

$$\hat{\rho}_0 = (1/N) \sum_k \hat{\rho}_k \quad (51)$$

We will prepare a system by a preparation  $Z$  consisting in applying preparations  $Z_1, Z_2, \dots, Z_N$  consecutively and repeatedly; in other words, we will form a quantum ensemble in which the  $k + nN$  members, for each  $k$  ( $k = 1, 2, \dots, N$ ) and for  $n = 0, 1, 2, \dots$ , are prepared by applying preparation  $Z_k$ . It is clear that the act of periodically applying preparations  $Z_1, Z_2, \dots, Z_N$  is under the control of the preparer and does not represent any known quantum phenomenon. By definition, however, measurements on the ensemble of preparation  $Z$  will result in a canonical operator  $\hat{\rho}_0$ , and measurements on the  $k + nN$  members, for each  $k$  and  $n = 0, 1, 2, \dots$ , will result in statistics that cannot be represented by a canonical operator  $\hat{\rho}_0$ ; in effect, preparation  $Z$  results in a quantum ensemble that can be subdivided

prior to measurement into  $N$  subensembles each of which is characterized by a density operator different than the canonical operator of  $Z$ . According to the present theory, each of these subensembles must represent a nonstable state and, therefore, must have a positive adiabatic availability (Theorem 3.7, Part IIa). It follows that the work that could be extracted adiabatically from the system prepared according to preparation  $Z$  is at least the sum of these positive adiabatic availabilities.

Thus, we conclude that a stable preparation corresponding to a canonical operator  $\hat{\rho}_0$  and preparation  $Z$  are characterized by the same density operator, and yet they result in adiabatic availabilities that can be substantially different.

It is clear that in a unified theory of mechanics and thermodynamics this conclusion creates an inconsistency. For given values of parameters, adiabatic availability is uniquely determined by the values of energy and entropy of the system, which in turn are uniquely determined by the density operator. Yet, preparation  $Z$  and the stable preparation have different availabilities, although these two preparations result in the same density operator  $\hat{\rho}_0$ . This inconsistency has physically unacceptable consequences, and leads to the need for an explicit operational circumscription of the terms *identically prepared systems* or *unambiguous preparation associated with a state*.

### 4.3. Definition of Unambiguous Preparation

We shall define a *preparation as unambiguous* and the resulting ensemble as consisting of *identically prepared systems* that are in a state  $\hat{\rho}$  and that are subject to the predictions of the present unified theory if and only if the subdivision of the ensemble prior to measurement into two or more subensembles, according to any conceivable operational rule, will always result in each subensemble being in the same state  $\hat{\rho}$ ; in other words, the statistics of measurements performed on any subensemble after subdivision will be representable by the same density operator  $\hat{\rho}$  as the statistics of the overall ensemble. If measurements performed on the subensembles after subdivision yield statistics that are represented by density operators that are different than that of the overall ensemble, the preparation will be called *ambiguous*.

These definitions are motivated by the stable-equilibrium postulate and their importance will become evident from the subsequent discussion.

### 4.4. Theorem

Given an ensemble of systems prepared by a preparation  $Z$  and consisting of several subensembles, the preparation is unambiguous if: (1) measurements performed from time to time on each system of the ensemble

and on each system of the subensembles yield results that are statistically independent; and (2) the joint probabilities for such results are the same for both the ensemble and the collection of the subensembles.

Consistent with the ideas of Margenau<sup>(19,20)</sup> and Park (Ref. 2, p. 221) this theorem presumes that single measurements do not fix the state of an entire ensemble, i.e., that the projection postulate of von Neumann is invalid.

*Proof:* We will assume that prior to measurement two subensembles 1 and 2 are identified with density operators  $\hat{\rho}_1$  and  $\hat{\rho}_2$  ( $\hat{\rho}_1 \neq \hat{\rho}_2 \neq \hat{\rho}$ ) and fractional contributions  $w_1$  and  $w_2$  ( $w_1 + w_2 = 1$ ), respectively, so that the density operator  $\hat{\rho}$  of the ensemble is given by the relation

$$\hat{\rho} = w_1\hat{\rho}_1 + w_2\hat{\rho}_2 \tag{52}$$

After subdivision, sequential measurements in each of the two subensembles at times  $t_a$  and  $t_b$  would yield the density operators  $\hat{\rho}_1(t_a)$  and  $\hat{\rho}_1(t_b)$  and  $\hat{\rho}_2(t_a)$  and  $\hat{\rho}_2(t_b)$ , respectively. Because of the statistical independence, joint probabilities for measurement results of a given observable at times  $t_a$  and  $t_b$  would be derivable from the operator  $\hat{R}_s$  given by the relation

$$\hat{R}_s = w_1\hat{\rho}_1(t_a)\hat{\rho}_1(t_b) + w_2\hat{\rho}_2(t_a)\hat{\rho}_2(t_b) \tag{53}$$

namely as weighted averages of joint probabilities obtained from the two subensembles. On the other hand, measurement results of quantum mechanical observables of the overall ensemble at times  $t_a$  and  $t_b$  yield the overall density operators

$$\hat{\rho}(t_a) = w_1\hat{\rho}_1(t_a) + w_2\hat{\rho}_2(t_a), \quad \hat{\rho}(t_b) = w_1\hat{\rho}_1(t_b) + w_2\hat{\rho}_2(t_b) \tag{54}$$

Again, because of the statistical independence, joint probabilities for measurement results of a given observable at times  $t_a$  and  $t_b$  would be derivable from the operator  $\hat{R}_e$  given by the relations

$$\begin{aligned} \hat{R}_e &= \hat{\rho}(t_a)\hat{\rho}(t_b) \\ &= w_1^2\hat{\rho}_1(t_a)\hat{\rho}_1(t_b) + w_2^2\hat{\rho}_2(t_a)\hat{\rho}_2(t_b) \\ &\quad + w_1w_2[\hat{\rho}_1(t_a)\hat{\rho}_2(t_b) + \hat{\rho}_1(t_b)\hat{\rho}_2(t_a)] \end{aligned} \tag{55}$$

Comparing Eqs. (53) and (55), we see that equality between  $\hat{R}_s$  and  $\hat{R}_e$  is achieved if and only if

$$\hat{\rho} \equiv \hat{\rho}_1 \equiv \hat{\rho}_2 \tag{56}$$

namely, if and only if preparation  $Z$  is unambiguous, otherwise  $\hat{R}_s \neq \hat{R}_e$ . Inequality between  $\hat{R}_s$  and  $\hat{R}_e$  implies the existence of correlations between measurements at  $t_a$  and  $t_b$ .

The equality of the joint probability operators  $\hat{R}_s$  and  $\hat{R}_e$  provides an operational criterion for deciding whether a preparation is unambiguous or ambiguous. If this equality is ascertained for all possible subdivisions of the ensemble into subensembles, then all systems in the ensemble are identically prepared according to an unambiguous preparation that cannot be subdivided into other unambiguous preparations. It is clear that operationally the density operator (pure or mixed) resulting from an unambiguous preparation does not have the ambiguities that revealed the inconsistency of Section 4.2. The state represented by a  $\hat{\rho}$  of an unambiguous preparation is the type of state that is subject to the predictions of the unified theory presented in this work.

When  $\hat{R}_s$  differs from  $\hat{R}_e$ , then the preparation is ambiguous and the density operator  $\hat{\rho}$  cannot be used to represent a state because the ensemble consists of more than one state. For example, if the preparation for  $\hat{\rho}$  consists of two unambiguous preparations  $\hat{\rho}_1$  and  $\hat{\rho}_2$  so that  $\hat{\rho} = w_1\hat{\rho}_1 + w_2\hat{\rho}_2$ , then one subensemble in the overall ensemble is in state  $\hat{\rho}_1$  and the other in state  $\hat{\rho}_2$ . Accordingly, the overall ensemble cannot be regarded as being in state  $\hat{\rho}$ . Such a  $\hat{\rho}$  and the associated ensemble of systems are not subject to the predictions of the stable-equilibrium postulate. Ambiguous  $\hat{\rho}$ 's and the associated ensembles may be analyzed by means of information theory, as will be discussed in a future communication.

#### 4.5. Theorem

Given an ensemble of identical systems having a Hamiltonian operator  $\hat{H}$  and a density operator  $\hat{\rho}$ , and consisting of two or more subensembles each of which is prepared by means of an unambiguous preparation, the entropy defined in terms of available energy is either equal to  $-k \text{Tr}(\hat{\rho} \ln \hat{\rho})$  if the preparations of the subensembles are identical, or smaller than  $-k \text{Tr}(\hat{\rho} \ln \hat{\rho})$  if the preparations of the subensembles are different.

*Proof:* We will consider two subensembles 1 and 2, having density operators  $\hat{\rho}_1$  and  $\hat{\rho}_2$ , respectively, each prepared by means of an unambiguous preparation and such that  $\hat{\rho}$  is given by Eq. (52). Prior to any measurement, an observer could subdivide the ensemble into the two subensembles. Then he would establish experimentally (either through measurements of adiabatic availability or through measurements of available energy) entropies  $S(\hat{\rho}_1) = -k \text{Tr}(\hat{\rho}_1 \ln \hat{\rho}_1)$  and  $S(\hat{\rho}_2) = -k \text{Tr}(\hat{\rho}_2 \ln \hat{\rho}_2)$  for the two subensembles, and would assign an average entropy  $S_{\text{av}}$  to the overall ensemble given by the relation

$$S_{\text{av}} = w_1 S(\hat{\rho}_1) + w_2 S(\hat{\rho}_2) \quad (57)$$

On the other hand, the observer could also use the density operator  $\hat{\rho} = w_1\hat{\rho}_1 + w_2\hat{\rho}_2$  obtained from these measurements to compute the quantity  $-k \text{Tr}(\hat{\rho} \ln \hat{\rho})$ . It can be shown<sup>(21)</sup> that if and only if  $\hat{\rho}_1 \equiv \hat{\rho}_2 \equiv \hat{\rho}$  then and only then

$$S_{av} = -k \text{Tr}(\hat{\rho} \ln \hat{\rho}) \quad (58)$$

Otherwise

$$S_{av} < -k \text{Tr}(\hat{\rho} \ln \hat{\rho}) \quad (59)$$

These results can be easily extended to more than two subensembles. Equations (58) and (59) are formal proofs of Theorem 4.5, and provide another operational criterion for distinguishing between unambiguous and ambiguous preparations.

#### 4.6. An Analogy from Probability Theory

The concept of an unambiguous preparation presented in Sections 4.3–4.5 may be illustrated by means of a simple example from probability theory. Suppose that we cut a large number of metallic rods each appearing to have the same length, and that we wish to verify through measurements if indeed the cutting process results in identical lengths. Suppose further, however, that because of either the available measurement technique or some inherent characteristics of the rods, or both, the results of the measurements include a random but statistically unique error so that, even if all the rods were cut to identical lengths, the measurement results would be dispersed. Under these conditions, the question arises: Is it possible to determine whether the rods were prepared by the same cutting procedure?

We may answer this question by proceeding as follows. First, we measure the lengths of the set of all the rods, make a graph of frequency vs. length, and find the average length. Next we divide the rods into two subsets: one consisting of the rods having measured lengths longer than the average, and the other consisting of the rods having lengths shorter than the average. Then we repeat the length measurements and make frequency vs. length graphs for each subset. Elementary probability theory indicates that if indeed all the rods were prepared by the same cutting procedure and the observed dispersions were solely due to random effects not associated with the cutting procedure, then the frequency graphs corresponding to the two subsets would be identical. On the other hand, if the rods were not prepared by the same cutting procedure, then the frequency graphs of the two subsets would not be identical. This example would be valid if the length of each rod were changing with time provided, of course, that the time evolution was the same for each rod.

#### 4.7. On Irreducible Dispersions

The criterion for unambiguous preparations given in Section 4.3 provides an operational means for distinguishing between dispersions of measurement results that are inherent in the nature of a system and those that are related to voluntary or involuntary incompleteness of experimentation. The former represent characteristics of a system that are beyond the control of an observer. They cannot be reduced by any means, including quantum mechanical measurement, short of processes that result in entropy transfer from the system to the environment. For pure states, these irreducible dispersions are, of course, the essence of Heisenberg's uncertainty principle. For mixed states, they limit the amount of energy that can be extracted adiabatically from the system.

Additional dispersions introduced by voluntary or involuntary incompleteness of experimentation represent inadequacies in the knowledge of observers. As such, though subject to improvement, they are not subject to the full prescriptions of the laws of physics.

The existence of irreducible dispersions associated with mixed states is required by Postulate 4, which expresses the basic implications of the second law of classical thermodynamics. Alternatively, the present work demonstrates that the second law is a manifestation of phenomena characteristic of irreducible quantal dispersions associated with the elementary constituents of matter.

The possibility of a relation between the second law (in the form of the impossibility of a Maxwellian demon) and irreducible dispersions associated with pure states (represented by Heisenberg's uncertainty principle) was suggested by Slater.<sup>(22)</sup> His suggestion was not adopted, however, because Demers<sup>(23)</sup> proved that dispersions associated with pure states are insufficient to account for the implications of the second law, especially with regard to heavy atoms at low pressures. In the present work we can relate the second law to quantal dispersions of mixed states because we have disclosed the existence of dispersions of mixed states that are irreducible.

#### 4.8. Remark on Large Systems

When systems having large numbers of degrees of freedom are in states not far from stable equilibrium, the products of probability distributions and degeneracy distributions that yield the frequencies of values of measurement results generally possess a single and extremely narrow peak.<sup>(24)</sup> The dispersions associated with such states are practically undetectable; in other words, repetitive measurements are not usually required in practice to determine expectation values. For example, for a system with many

degrees of freedom, the expectation value of the energy for a stable equilibrium state can be established with a great degree of confidence by means of a single measurement because the probability that a measurement would yield a value significantly different from the expectation value is extremely small. Moreover, the adiabatic availability of such a state can be established accurately by means of a single measurement.

Although undetectable in direct property measurements of large systems, the irreducible dispersions not only determine the value of  $\text{Tr}(\hat{\rho} \ln \hat{\rho})$  of large systems, but also relate causally to the large differences between energies and adiabatic availabilities that are consistently observed for certain states, such as stable equilibrium states. These dispersions play a key role in determining the modes of interaction of the system with others (for example, heat interactions), and introduce irreducible limitations in the behavior of the system.

## 5. CONCLUSIONS

The work presented in Parts I–III, though expressed only in terms of quantum states of ultimate possible detail, brings within a single theory both quantum mechanics and classical thermodynamics. In this theory the state of any system is described by means of probabilities that are inherent in the nature of the system and that are associated with measurement results obtained from an ensemble of systems of unambiguous preparation. Moreover, the second law of thermodynamics emerges as a fundamental law related to irreducible quantal dispersions of mixed states and applicable to systems of any size, including a single particle.

A key element of the theory is the statement of operational criteria for the distinction between ambiguous and unambiguous preparations (pure or mixed).

For unambiguous preparations, the theory reveals limitations on the amount of work that can be done by a system adiabatically and without net changes in parameters. These limitations are due to irreducible dispersions inherent in the state of the system. They are maximal when the dispersions correspond to a stable equilibrium state.

The theory indicates that a measure of the limitations is provided by the quantity  $S$  (Theorem 3.15, Part IIa) which has physical meaning and unique value for any state, stable equilibrium, equilibrium, or nonequilibrium. The larger the value of  $S$ , the smaller the amount of work that can be extracted adiabatically from the system. For any state the quantity  $S$  is called entropy because for stable equilibrium states it behaves like the entropy of classical thermodynamics.

Finally, the theory discloses the limited applicability of the known equation of motion. This equation is open to question not only for irreversible processes but also for many frequently encountered reversible processes.

## ACKNOWLEDGMENTS

We are greatly indebted to Dr. Joseph H. Keenan, Professor Emeritus at MIT, for his invaluable guidance, critical discussions, and thorough review of the manuscript. We are appreciative of helpful comments received from Prof. Stephen J. Kline, Stanford University, Prof. Henry Margenau, Yale University, Dr. Lothar W. Nordheim, Gulf General Atomic Company, Prof. James L. Park, Washington State University, and Dr. Stylianos J. Pezaris, Lincoln Laboratory MIT. Finally, we are thankful to Linda Croff and Fran Grande for their meticulous typing of several versions of the manuscript.

## REFERENCES

17. H. Margenau, *The Nature of Physical Reality* (McGraw-Hill, New York, 1950).
18. J. L. Park, *Am. J. Phys.* **36**, 211 (1968).
19. H. Margenau, *Philosophy of Science* **4**, 352 (1937); **25**, 23 (1958).
20. H. Margenau, *Philosophy of Science* **30**, 138 (1963).
21. E. H. Lieb and M. B. Ruskai, *Phys. Rev. Lett.* **30** (10), 434 (1973).
22. J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, New York, 1939).
23. P. Demers, *Can. J. Res.* **22**, 27 (1944); **23**, 47 (1945).
24. E. Schrödinger, *Statistical Thermodynamics* (Cambridge Univ. Press, London, 1946).