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Stochastic Equations for Nonequilibrium Processes*†

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A system of weakly interacting particles is described by a time-dependent joint probability distribution in the occupation numbers of the individual particle states. The "master" equation for the distribution is obtained by considering the time evolution of the system as a Markoff process with transition probabilities per unit time given by first-order quantum mechanical perturbation theory. This is done for particles obeying classical and quantum statistics. The resulting equations include the usual rate equations for the average occupation numbers as special cases; but they also yield all higher moments and correlations in the occupation numbers. The general solution and its properties are

discussed for the case in which a relaxing subsystem interacts via binary collisions with a larger system having a fixed but not necessarily thermal distribution. The explicit solution for the joint distribution in occupation numbers for all time is constructed for the case of identical harmonic oscillators which have an arbitrary initial distribution. These interact via binary collisions with a reservoir of similar oscillators, the coupling being linear in each oscillator coordinate. This model is also generalized and solved for a case in which the number of interacting particles is not conserved.

I. INTRODUCTION

A BASIC problem of theoretical physics is that of describing the approach to equilibrium, from an arbitrary initial state, of a system composed of a large number of interacting particles. Ever since the classic work of Boltzmann, it has been recognized¹ that statistical, as well as dynamical, considerations must play an important role in describing the change in time of such systems. In this paper we shall characterize the state of the whole system at any time by a joint probability distribution (JPD), $P(n_1, \dots, n_i, \dots; t)$, for the occupation numbers, n_i , of the individual particle states, i . Further, assuming that the change of state of the system may be described as a Markoff stochastic process, we shall obtain the "master equation"² ap-

propriate to such a process for the systems under consideration. The transition probabilities per unit time are taken from first-order quantum mechanical perturbation theory.

This procedure leaves open the question of how far such probabilistic equations are derivable from the exact quantum dynamical equations of motion. Implicit in our approach is the assumption (which has been used, for example, by Pauli³ in his derivation of the H -theorem) that the occupation numbers remain good quantum numbers for all time. Since the occupation numbers correspond to diagonal elements of a density matrix, it is not obvious why, during the course of time, nondiagonal matrix elements should not become equally important. Pauli eliminated them by invoking random phase averages at all times. Considerable progress has been made recently in clarifying this situation, mainly through the work of Van Hove,⁴ Brout,⁵ and Prigogine⁶ which provides both a critique of and a justification for the use of a master equation. In particular, Van Hove has succeeded in deriving the

* A preliminary account of this work was given in Bull. Am. Phys. Soc. 4, 15 (1959).

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¹ P. Ehrenfest and T. Ehrenfest, *Encyclopaedia der Math. Wissenschaften*, Vol. IV, pt. 32, 1911.

² This terminology is due to G. E. Uhlenbeck. It refers to the differential equation governing the time dependence of the JPD of the occupation numbers for a Markoff process. See, for example, G. E. Uhlenbeck, *Higgins Lectures*, Princeton University, 1954 (unpublished).

³ W. Pauli, *Festschrift zum 60 Geburtstag A. Sommerfelds* (S. Hirzel, Leipzig, 1928), p. 30.

⁴ L. Van Hove, *Physica* 21, 517 (1955); 23, 441 (1957).

⁵ R. Brout, *Physica* 22, 509 (1956).

⁶ I. Prigogine and co-workers in numerous papers in *Physica* 23, 24, and 25 (1957-1959).

master equation, under certain conditions, as a valid first approximation from the quantum mechanical equations of motion for a system of a large number of weakly interacting particles.

The understanding of the approach to equilibrium described by using the master equation has been greatly aided by the rapid development of the theory of stochastic processes.⁷⁻¹¹ On the one hand, general theorems have been proved which establish such relevant results as the existence, for a wide class of processes, of a unique stationary distribution to which a system will relax irrespective of its initial distribution. On the other hand, exact treatments of various special cases, i.e., models, have been given which have provided greater physical insight into the statistical behavior of systems approaching equilibrium. Indeed, although the instructiveness of such models has long been appreciated,^{12,13} it is only in recent years that even the simpler schematic models (such as the Ehrenfests' "dog-flea"¹² and "wind-tree" models) have been treated adequately.^{14,15}

This paper is a contribution in the latter direction, namely, that of delving more deeply into the consequences of the probabilistic formulation of relaxation phenomena. In Sec. II, we set up master equations for the JPD (joint probability distribution) in the occupation numbers for the cases in which the interacting particles obey classical or quantum statistics.¹⁶ Then in Sec. III, we exhibit some general consequences of these equations when the interacting particles may be considered to consist of two sets, one of which (the relaxing set) is free to change its distribution, while the other (the reservoir set) has its distribution maintained constant in time by some external agency.

In Sec. IV, a complete solution is given for a special physical situation: the relaxation of an arbitrarily excited gas of harmonic oscillators interacting via binary collisions with a (not necessarily thermal) reservoir of similar oscillators. Although this process is

of considerable interest in the study of collisional and radiative relaxation of vibrationally excited gases, and has been treated in this connection by Shuler,¹⁷ Montroll,¹⁸ and Rubin,¹⁹ we shall here be concerned with it solely as a model for which one can exhibit in detail the occupation number JPD which describes the approach to equilibrium.

Finally, in Sec. V, a generalization of this model is solved in which the number of relaxing oscillators is no longer kept constant, thus allowing for the possibility of formation and dissociation of diatomic molecules.

The essential point in our development which makes possible a more complete statistical description of relaxation phenomena than that given by the conventional rate equations²⁰ is this: the latter are equations for the average occupation numbers, \bar{n}_i . However, the n_i are random variables and we determine their joint distribution $P(n_1, n_2, \dots; t)$ as a function of time. In obtaining the master equation governing this JPD, the same quantum mechanical transition probabilities are used as in obtaining the usual rate equations. These latter, of course, follow from our master equation by suitable averaging. But from our JPD, $P(n_1, n_2, \dots; t)$, we can obtain in addition all higher moments, e.g., correlations, $\langle n_i n_j \rangle_{av}$,²¹ and fluctuations, $\langle (n_i - \bar{n}_i)^2 \rangle_{av}$, in the occupation numbers for all time.

II. MASTER EQUATION FOR THE PROBABILITY DISTRIBUTION AND ITS GENERATING FUNCTION

A. The Master Equation

In this section we derive the master equation for both classical (M. B.) and quantum (B. E. and F. D.) statistics and deduce from it the associated equation for the generating function of the JPD.

This joint distribution, $P(\langle n \rangle; t) \equiv P(n_1, n_2, \dots; t)$, satisfies

$$P(\langle n \rangle; t+dt) = \sum_{\langle m \rangle} P(\langle m \rangle; t) P(\langle m \rangle; t \rightarrow \langle n \rangle; t+dt), \quad (2.1)$$

where $P(\langle m \rangle; t \rightarrow \langle n \rangle; t+dt)$ is the conditional probability of finding the set of occupation numbers $\langle n \rangle$ at

¹⁷ K. E. Shuler, J. Phys. Chem. **61**, 849 (1957).

¹⁸ E. W. Montroll and K. E. Shuler, J. Chem. Phys. **26**, 454 (1957).

¹⁹ R. J. Rubin and K. E. Shuler, J. Chem. Phys. **26**, 137 (1957).

²⁰ See references 17-19 for the rate equations describing interacting harmonic oscillators. The rate equations for the average occupation numbers are used in most kinetic treatments of entropy or the H -theorem. See, for example, R. Tolman, *Principles of Statistical Mechanics* (Clarendon Press, Oxford, 1938); D. Ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954), Appendix I; or W. Pauli, reference 3. Such equations are also standard in the theory of paramagnetic relaxation, e.g., N. Bloembergen, R. V. Pound, and E. M. Purcell, Phys. Rev. **73**, 679 (1948).

²¹ Because of typesetting limitations, the symbol " $\langle \rangle_{av}$ " is used in place of a bar to indicate averages of products of random variables.

⁷ M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945).

⁸ S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

⁹ M. Kac, *Probability and Related Topics in Physical Sciences* (Interscience Publishers, New York, 1959).

¹⁰ J. E. Moyal, J. Roy. Stat. Soc. **B11**, 150 (1949).

¹¹ References 6-10 are concerned mainly with physical applications. More mathematical treatments are given in the books: W. Feller, *Introduction to Probability Theory* (John Wiley & Sons, Inc., New York, 1957); M. S. Bartlett, *Introduction to Stochastic Processes* (Cambridge University Press, New York, 1955); J. S. Doob, *Stochastic Processes* (John Wiley & Sons, Inc., New York, 1953).

¹² P. Ehrenfest and T. Ehrenfest, Physik. Z. **8**, 311 (1907).

¹³ M. v. Smoluchowski, Physik. Z. **17**, 557 (1916).

¹⁴ M. Kac, Am. Math. Monthly **54**, 369 (1947).

¹⁵ A. J. F. Siegert, Phys. Rev. **76**, 1708 (1949).

¹⁶ This formulation of the relaxation problem is due to Siegert and Moyal (references 15 and 10), who, however, were primarily concerned with the method rather than with obtaining explicit solutions for specific models. Their work is noteworthy in giving the Boltzmann Stosszahlansatz a proper probabilistic formulation for both classical and quantum statistics; our work is a direct continuation of theirs.

time $t+dt$, given the set $\langle m|$ at t . The summation extends over all possible sets $\langle m|$ of the occupation numbers. We restrict ourselves to processes with stationary transition probabilities so that

$$P(\langle m|; t \rightarrow \langle n|; t+dt)$$

depends only on the time difference dt and not on t .

Assuming that the limit exists, we define

$$Q(\langle m| \rightarrow \langle n|) = \lim_{dt \rightarrow 0} \left[\frac{P(\langle m|; t \rightarrow \langle n|; t+dt) - \prod_i \delta(n_i, m_i)}{dt} \right], \quad (2.2)$$

where $\delta(n_i, m_i)$ is unity if $n_i = m_i$ and is zero otherwise. We note that Q satisfies

$$Q(\langle m| \rightarrow \langle n|) \geq 0 \quad \text{for} \quad \langle m| \neq \langle n|, \quad (2.3a)$$

and

$$Q(\langle m| \rightarrow \langle m|) = - \sum_{\langle n| \neq \langle m|} Q(\langle m| \rightarrow \langle n|). \quad (2.3b)$$

These relations follow from

$$P(\langle m| \rightarrow \langle n|; t) \equiv P(\langle m|; t_0 \rightarrow \langle n|; t_0+t) \geq 0, \quad (2.4a)$$

and

$$\sum_{\langle n|} P(\langle m| \rightarrow \langle n|; t) = 1. \quad (2.4b)$$

If $\langle m| \neq \langle n|$, then $Q(\langle m| \rightarrow \langle n|)$ is just the probability per unit time that the system undergoes in a transition from a state with the set of occupation numbers $\langle m|$ to another with the set of occupation numbers $\langle n|$.

The matrix elements $Q(\langle m| \rightarrow \langle n|)$ differ from zero only when the conservation laws are satisfied. From (2.1) and (2.2) one gets the master equation

$$\frac{\partial P(\langle n|; t)}{\partial t} = \sum_{\langle m|} P(\langle m|; t) Q(\langle m| \rightarrow \langle n|), \quad (2.5)$$

or, in more succinct notation,

$$\partial \langle P(t) | / \partial t = \langle P(t) | Q, \quad (2.5a)$$

where $\langle P(t) |$ is a row vector with elements $P(\langle n|; t)$ and Q is the matrix whose rows and columns are indexed by the sets of occupation numbers $\langle m|$ and $\langle n|$, respectively. The formal solution to (2.5a) is

$$\langle P(t) | = \langle P(0) | e^{Qt}, \quad (2.6)$$

where $\langle P(0) |$ is the row vector of the arbitrary initial distribution, $P(\langle n|; 0)$. This deceptively simple-looking formal solution is of little use in practice since it can entail exponentiating an infinite dimensional matrix if the number of states is infinite. Indeed, the master equation (2.5) then represents an infinite set of ordinary differential equations, one for each possible set of occupation numbers. The solution of this set of equa-

tions for the JPD, with the integral-valued arguments n_i , is often facilitated by transforming from P to a probability generating function (PGF), Φ , defined by the equation

$$\Phi(z_1, z_2, \dots; t) \equiv \Phi(|z|; t) = \sum_{\langle n|} z_1^{n_1} z_2^{n_2} \dots P(\langle n|; t). \quad (2.7)$$

Equation (2.7) determines the one-to-one correspondence between Φ and P . A formal advantage of working with Φ is that it is an analytic function in each of its continuous-valued arguments z_i ; it is thus amenable to the methods of analysis rather than to those of algebra. In fact it will be shown below that $\Phi(|z|; t)$ satisfies a single partial differential equation. One also readily obtains from Φ all of the moments of $P(\langle n|; t)$ as well as any desired marginal distributions by noting that the summing of P over all values of n_i , for any i , is equivalent to setting $z_i = 1$ in Φ . Thus, using the definition of probability and Eq. (2.7), we find that

$$\Phi(|z|; t)_{z_1=z_2=\dots=1} = 1, \quad (2.8)$$

and that the moments of the occupation numbers are given by

$$\langle n_1 n_2 \dots n_k \rangle_{av} = \left[z_1 \frac{\partial}{\partial z_1} z_2 \frac{\partial}{\partial z_2} \dots z_k \frac{\partial}{\partial z_k} \Phi \right]_{z_1=z_2=\dots=1}. \quad (2.9)$$

A marginal distribution such as, say, $P(n_1, n_2; t)$ is just the set of coefficients of $z_1^{n_1} z_2^{n_2}$ in the series expansion of $\Phi(z_1, z_2; t)$, the marginal PGF (probability generating function), which one gets from (2.7) by setting all $z_i = 1$, except z_1 and z_2 .

The equation satisfied by Φ follows from (2.5):

$$\frac{\partial \Phi}{\partial t} = \sum_{\langle n|} \sum_{\langle m|} P(\langle m|; t) Q(\langle m| \rightarrow \langle n|) \prod_i z_i^{n_i}. \quad (2.10)$$

We define

$$\Gamma(\langle m|; |z|) \equiv \sum_{\langle n|} Q(\langle m| \rightarrow \langle n|) \prod_i z_i^{n_i - m_i} = \sum_{\langle n-m|} Q'(\langle m|; \langle n-m|) \prod_i z_i^{n_i - m_i}, \quad (2.11)$$

where

$$Q'(\langle m|; \langle n-m|) \equiv Q(\langle m| \rightarrow \langle n-m|).$$

On using (2.3b), this can also be written as

$$\Gamma(\langle m|; |z|) = \sum_{\langle m-n| \neq \langle 0|} Q'(\langle m|; \langle n-m|) \times \left[\prod_i z_i^{n_i - m_i} - 1 \right]. \quad (2.12)$$

The right-hand side of (2.10) now becomes

$$\sum_{\langle m|} \Gamma(\langle m|; |z\rangle) \left(\prod_i z_i^{m_i} \right) P(\langle m|; t) \\ = \Gamma(\langle z\partial/\partial z|; |z\rangle) \Phi(|z\rangle; t), \quad (2.13)$$

where the derivatives act only on $\Phi(|z\rangle; t)$. (We use this notation to eliminate the explicit dependence on the integral-valued occupation numbers.) Hence (2.10) may be written as the symbolic operator equation

$$\frac{\partial \Phi(|z\rangle; t)}{\partial t} = \Gamma(\langle z\partial/\partial z|; |z\rangle) \Phi(|z\rangle; t). \quad (2.14)$$

This is the fundamental equation which we shall employ in the following sections.²²

Before proceeding further, we must specify in more detail the transition probability matrix $Q(\langle m| \rightarrow \langle n|)$. We shall assume that the changes in the state of the whole system take place through events in which the occupation numbers of several of the states i change simultaneously. For an event in which p particles disappear from states i_1, i_2, \dots, i_p and q particles appear in states k_1, k_2, \dots, k_q (the occupation numbers of all other states remaining unchanged), we take the transition probability per unit time to be given

by

$$Q(n(i_1), \dots, n(i_p); n(k_1), \dots, n(k_q) \rightarrow \\ n(i_1)-1, \dots, n(i_p)-1; n(k_1)+1, \dots, n(k_q)+1) \\ = A(i_1, \dots, i_p; k_1, \dots, k_q) n(i_1) \dots n(i_p) \\ \times [1+\theta n(k_1)] \dots [1+\theta n(k_q)]. \quad (2.15)$$

Here $n(k_q)$ is the occupation number of the state k_q ; and $\theta=0, +1$, and -1 apply, respectively, to particles obeying classical (M. B.), B. E., and F. D. statistics. In the latter two cases the expression (2.15) follows from first order quantum mechanical perturbation theory²³; the coefficients $A(i_1, \dots, i_p; k_1, \dots, k_q)$ are the squares of the absolute values of matrix elements of the interaction term in the Hamiltonian between initial and final states of the system. For systems, like a gas at low density, that are adequately described by classical statistics, (2.15) represents the familiar Boltzmann Stosszahlansatz. In this case $q=p$, and the factor $A(i_1, \dots, i_p; k_1, \dots, k_p)$ can be interpreted as the probability per collision for the transition $(i_1, \dots, i_p \rightarrow k_1, \dots, k_p)$ while the product $n(i_1) \dots n(i_p)$ is proportional to the probability per unit time for a collision involving p particles in the initial states i_1, i_2, \dots, i_p .

Equation (2.15) is applicable only to transitions in which the states involved change their occupation numbers by unity. However, in general, there can be transitions in which the occupation numbers change by arbitrary amounts. The corresponding transition probability per unit time is

$$Q(n(i_1), \dots, n(i_p); n(k_1), \dots, n(k_q) \rightarrow n(i_1)-r(i_1), \dots, n(i_p)-r(i_p); n(k_1)+r(k_1), \dots, n(k_q)+r(k_q)) \\ = A(i_1, \dots, i_p; k_1, \dots, k_q | r(i_1), \dots, r(i_p); r(k_1), \dots, r(k_q)) \left(\prod_{j=1}^p \{n(i_j)[n(i_j)-1] \dots [n(i_j)-r(i_j)+1]\} \right) \\ \times \prod_{j=1}^q \{[1+\theta n(k_j)][1+\theta(n(k_j)+1)] \dots [1+\theta(n(k_j)+r(k_j)-1)]\}. \quad (2.16)$$

In particular,

$$A(i_1, \dots, i_p; k_1, \dots, k_q | 1, \dots, 1; 1, \dots, 1) = A(i_1, \dots, i_p; k_1, \dots, k_q),$$

and in this case (2.16) reduces to (2.15). From the definition of Γ it now follows that

$$\Gamma(\langle n|; |z\rangle) = \sum_{p,q} \sum_{\substack{r(i_1), \dots, r(i_p), \\ r(k_1), \dots, r(k_q)}} \sum'_{\substack{i_1, \dots, i_p, \\ k_1, \dots, k_q}} A(i_1, \dots, i_p; k_1, \dots, k_q | r(i_1), \dots, r(i_p); r(k_1), \dots, r(k_q)) \\ \times \left(\prod_{j=1}^p [z(i_j)]^{-r(i_j)} \right) \left(\prod_{j=1}^q [z(k_j)]^{r(k_j)} - 1 \right) \left(\prod_{j=1}^p \{n(i_j)[n(i_j)-1] \dots [n(i_j)-r(i_j)+1]\} \right) \\ \times \prod_{j=1}^q \{[1+\theta n(k_j)][1+\theta(n(k_j)+1)] \dots [1+\theta(n(k_j)+r(k_j)-1)]\}, \quad (2.17)$$

where the prime on the summation sign indicates that in summing over all single particle states no two of the indices $i_1, \dots, i_p, k_1, \dots, k_q$ should be taken equal

in the same term, and no event should be counted more than once. To be consistent with lowest order perturbation theory

²² Equations of this form were first introduced in this context by Moyal and Bartlett; see references 10 and 11.

²³ See Tolman's book, reference 20, Sec. 100, or D. I. Blochinzev, *Osnovi Kvantovoi Mekhaniki* (State Publishing House, Moscow, 1949), Sec. 115 (in Russian).

bation theory, one should retain only the terms of lowest order in the expansion (2.17) of Γ .

It may be noted that the sum over all sets of final state occupation numbers appearing in the definition (2.11) of Γ is equivalent to the sum over all transitions of a given type [characterized by fixed values of $p, q, r(i_1), r(i_2), \dots, r(i_p), r(k_1), r(k_2), \dots, r(k_q)$ —i.e., the sum over states in (2.17)—followed by a sum over all types of transitions.

Substitution of (2.17) into (2.14) now yields the

$$\begin{aligned} \frac{\partial \Phi}{\partial t} = & \frac{1}{4} \sum_{i,j,k,l} A_{ij}{}^{kl} (z_k z_l - z_i z_j) [\partial_i \partial_j (1 + \theta z_k \partial_k) (1 + \theta z_l \partial_l)] \Phi + \frac{1}{2} \sum_{i,k,l} A_{ii}{}^{kl} (z_k z_l - z_i^2) [\partial_i^2 (1 + \theta z_k \partial_k) (1 + \theta z_l \partial_l)] \Phi \\ & + \frac{1}{2} \sum_{i,j,k} A_{ij}{}^{kk} (z_k^2 - z_i z_j) [\partial_i \partial_j (1 + \theta z_k \partial_k) (1 + \theta (z_k \partial_k + 1))] \Phi \\ & + \sum_{i,k} A_{ii}{}^{kk} (z_k^2 - z_i^2) [\partial_i^2 (1 + \theta z_k \partial_k) (1 + \theta (z_k \partial_k + 1))] \Phi \equiv \Gamma_2(\langle z \partial / \partial z |; | z \rangle) \Phi, \quad (2.18) \end{aligned}$$

where $\partial_i \equiv \partial / \partial z_i$ and $A_{ij}{}^{kl} \equiv A(i, j; k, l)$. The factors $\frac{1}{4}$ and $\frac{1}{2}$ compensate for multiple counting of identical events. (In this equation and in the sequel, if any pair of summation indices are equal in a given term, then this term is excluded.)

In the case of a gas, if the individual particle states of definite momentum (and energy) are labelled by i, j, \dots , then the coefficients $A_{ij}{}^{kl}$ vanish whenever $i=j$ or $k=l$, by energy-momentum conservation, so that the last three terms in (2.18) drop out, reducing the equation to

$$\frac{\partial \Phi}{\partial t} = \frac{1}{4} \sum_{i,j,k,l} A_{ij}{}^{kl} (z_k z_l - z_i z_j) \times [\partial_i \partial_j (1 + \theta z_k \partial_k) (1 + \theta z_l \partial_l)] \Phi. \quad (2.19)$$

This is the form considered by Moyal¹⁰ and by Siegert¹⁵ (with $\theta=0$). However there are systems for which this simplification is not applicable. For example, in a gas of diatomic molecules whose vibrational states are labelled by i, j, \dots , it is possible for two molecules which are initially in the same vibrational state to transfer energy during a collision and go to different final states so that (2.18) rather than (2.19) is required.

No general solution is known for Eq. (2.18) or (2.19). Siegert¹⁵ has obtained a solution of (2.19) for a 2-state system for all time. Moyal¹⁰ has obtained a time-independent solution to (2.19) by assuming statistical independence of the occupation numbers of the various states. His solution corresponds to the grand canonical ensemble equilibrium distribution with the average occupation numbers \bar{n}_i given by

$$\bar{n}_i / (1 + \theta \bar{n}_i) = C e^{-\beta \epsilon_i}, \quad (2.20)$$

where ϵ_i is the energy of a particle in state i , and C is a normalization constant. [As usual, $\beta = (kT)^{-1}$.]

partial differential equation for Φ equivalent to the master equation (2.5) for P .

In the sequel we will be concerned with the simple case in which interactions between particles occur exclusively through binary collisions. Then only four types of terms survive in (2.17), namely those for which

$$\left\{ \begin{array}{l} p=2, r(i_1)=r(i_2)=1 \\ \text{or } p=1, r(i_1)=2 \end{array} \right\} \quad \text{and} \quad \left\{ \begin{array}{l} q=2, r(k_1)=r(k_2)=1 \\ \text{or } q=1, r(k)=2 \end{array} \right\}.$$

The resulting equation for Φ is

In Sec. III we shall specialize Eq. (2.19) still further so as to be able to exhibit a solution for all time for the harmonic oscillator problem of references 17–19.

B. Rate Equations

By taking suitable derivatives of the PGF equation (2.18) or (2.19), and then setting all the z 's equal to unity according to (2.9), one can obtain rate equations for the various moments of the occupation numbers. In particular, the equation one gets for the rate of change of the averages, \bar{n}_i , is not the rate equation commonly used in transport theory²⁴ or in discussions of the H -theorem.³ To exhibit the essential difference, and the additional assumptions necessary for the conventional equations to be valid, we write down first the rate equation one gets from (2.19) for the M.B. case ($\theta=0$)²⁵:

$$\frac{d\bar{n}_k}{dt} = \frac{1}{2} \sum_{i,j,l} [A_{ij}{}^{kl} \langle n_i n_j \rangle_{av} - A_{kl}{}^{ij} \langle n_k n_l \rangle_{av}]. \quad (2.21)$$

This equation relates the time variation of \bar{n}_k to the time-dependent correlations $\langle n_i n_j \rangle_{av}$. Similarly the rate of change of the latter depends on $\langle n_i n_j n_k \rangle_{av}$, etc. Hence, we obtain a hierarchy of interconnected equations. Only with the additional assumption

$$\langle n_i n_j \rangle_{av} = \bar{n}_i \bar{n}_j \quad (2.22)$$

does Eq. (2.21) reduce to the form of the (nonlinear) Boltzmann equation appropriate for the case of a spatially homogeneous gas with no external forces.

²⁴ E. A. Uehling and G. E. Uhlenbeck, Phys. Rev. 43, 552 (1933).

²⁵ See also Siegert, reference 15, Appendix II.

The corresponding equation to (2.21) for F. D. or B. E. particles is readily obtained from (2.19):

$$\frac{d\bar{n}_k}{dt} = \frac{1}{2} \sum_{i,j,l} [A_{ij}{}^{kl} \langle n_i n_j (1+\theta n_k) (1+\theta n_l) \rangle_{av} - A_{ki}{}^{jl} \langle n_k n_l (1+\theta n_i) (1+\theta n_j) \rangle_{av}]. \quad (2.23)$$

This equation will also not reduce to the Boltzmann form with the modified Stosszahlansatz (used in the transport theory of degenerate quantum gases²⁴) unless one makes the additional assumption²⁶:

$$\langle n_i n_j (1+\theta n_k) (1+\theta n_l) \rangle_{av} = \bar{n}_i \bar{n}_j (1+\theta \bar{n}_k) (1+\theta \bar{n}_l). \quad (2.24)$$

III. SYSTEMS IN INTERACTION WITH A RESERVOIR

A. General Properties

Let us suppose that the interacting particles of a system can be divided into two sets (subsystems): a relaxing set and a reservoir set. Assume that within each set the particles are all of the same kind, although the two sets do not necessarily consist of the same kind of particles or have the same statistics. However, we require that the energy level spacings of the particles in the two subsystems be compatible so that energy exchange is possible.

The number of particles in the reservoir set is, by definition, very large compared to that in the relaxing system. Consequently, in studying the change in the occupation number distribution of the relaxing set, only the interaction between particles of this set and those of the reservoir need be considered, the effect of interactions within the relaxing set being negligible in comparison. On the other hand, the occupation number distribution of the reservoir set is assumed to be unaffected by its interaction with the relaxing set, and its time dependence may be prescribed arbitrarily.

Such a decomposition is appropriate for many physical systems. Some examples are:

(i) a "Rayleigh Gas"²⁷ consisting of a dilute mixture of low mass atoms (relaxing set) with an arbitrary initial velocity distribution and a homogeneous spatial distribution within a vessel of much heavier atoms (reservoir) which are in thermal equilibrium;

(ii) a gas of identical diatomic molecules (reservoir), a small fraction of which (relaxing set) has been excited to various vibrational states by a transient source of radiation¹⁷⁻¹⁹;

(iii) a paramagnetic salt, with excited spin state populations (relaxing set) which are coupled to the lattice vibrations or phonons (reservoir).

It should be noted that the reservoir need not be thermal, i.e., it need not have an occupation number

distribution corresponding to some definite temperature. In fact, the reservoir need not even be stationary. For example, in (iii) the spin states with energy difference $h\nu$ are coupled to phonons of frequency ν whose population could be made anomalous (greater than the average appropriate for the temperature of the lattice bath) by pumping with an ultrasonic generator at the resonance frequency ν . The phonon distribution would then be neither thermal nor stationary.

1. Master Equation for the Relaxing System

We shall now derive the master equation for the relaxing system. We first note that there are now two sets of occupation numbers, one for the relaxing system and the other for the reservoir. We denote these by $\langle n|$ and $\langle n'|$, respectively, and we denote the PGF of their JPD by $\Phi(|z\rangle, |z'\rangle; t)$. Assuming binary collisions between particles, we find that Φ satisfies

$$\begin{aligned} \frac{\partial \Phi}{\partial t} = & \Gamma_2(\langle z \partial / \partial z | ; | z \rangle) \Phi \\ & + \Gamma_2(\langle z' \partial / \partial z' | ; | z' \rangle) \Phi + \sum_{i,j,k,l} (z_k z_l' - z_i z_j') \\ & \times A_{ij}{}^{kl} [\partial_i \partial_j' (1 + \theta z_k \partial_k) (1 + \theta z_l' \partial_l')] \Phi. \end{aligned} \quad (3.1)$$

(The right side may also contain terms representing the effect of any external agency which acts on the reservoir.) The operator Γ_2 is defined in (2.18) and is appropriate when only binary collisions occur. The three terms in (3.1) correspond, respectively, to collisions within the relaxing system, collisions within the reservoir, and collisions between particles of the relaxing system and those of the reservoir. The first of these can be ignored in virtue of the discussion at the beginning of this section. We also note that the assumption of statistical independence between the reservoir and the relaxing system allows us to write

$$\Phi(|z\rangle, |z'\rangle; t) = \Phi_S(|z\rangle; t) \Phi_R(|z'\rangle; t), \quad (3.2)$$

where Φ_S and Φ_R are the separate PGF's for the relaxing system and for the reservoir, respectively. Setting $|z'\rangle = |1\rangle$ in (3.1) and using (2.18), we find that the second term vanishes identically, yielding the following equation for Φ_S :

$$\begin{aligned} \frac{\partial \Phi_S(|z\rangle; t)}{\partial t} = & \sum_{i,j,k,l} A_{ij}{}^{kl} [\bar{n}_j'(t) + \theta' \langle n_j' n_l'(t) \rangle_{av}] \\ & \times (z_k - z_i) [\partial_i (1 + \theta z_k \partial_k)] \Phi_S(|z\rangle; t). \end{aligned} \quad (3.3)$$

Hence,

$$\frac{\partial \Phi(|z\rangle; t)}{\partial t} = \sum_{i,k} a_i{}^k (z_k - z_i) \partial_i (1 + \theta z_k \partial_k) \Phi(|z\rangle; t), \quad (3.4)$$

where

$$a_i{}^k = \sum_{j,l} A_{ij}{}^{kl} [\bar{n}_j'(t) + \theta' \langle n_j' n_l'(t) \rangle_{av}]. \quad (3.5)$$

²⁶ That this additional assumption is often implicitly made in applying (2.15) has also been pointed out by Blochinzhev, reference 23, p. 474.

²⁷ Lord Rayleigh, *Scientific Papers* (Cambridge University Press, New York, 1903), Vol. III, p. 473.

(We have dropped the subscript S on Φ since all future PGF's will refer to the relaxing system.) Equation (3.5) shows that only the means and correlations of the reservoir occupation numbers affect the relaxing system when the interaction is via binary collisions.

The form of the master equation for the PGF of the relaxing system as given by (3.4) is quite general (subject, however, to the statistical independence assumption): This form applies whatever the mechanism of interaction between particles, as long as only one relaxing particle is involved in a collision. The specific form of interaction, e.g., binary collisions, affects only the explicit structure of the a_i^k .

In a similar way one could obtain the master equation for the change with time of the reservoir PGF by setting $|z\rangle = |1\rangle$ in (3.1). However, we shall assume that the reservoir distribution is stationary. This can be realized physically to a very good approximation whenever (a) the number of reservoir particles is very much greater than those of the relaxing set, and (b) in the case of a stationary, but not thermal equilibrium distribution, the coupling of reservoir particles to the external agency is much stronger than their interaction with each other.

One can give a simple proof of, and thereby gain insight into, a general property of the a_i^k when the reservoir is thermal. *If the reservoir is in thermal equilibrium corresponding to a temperature $T=1/(\beta k)$ and if its particles are*

- (i) M. B. with $\bar{n}_i' = Ce^{-\beta \epsilon_i}$, or
- (ii) F. D. or B. E. with uncorrelated occupation numbers:

$$\bar{n}_i' / (1 + \theta' \bar{n}_i') = Ce^{-\beta \epsilon_i},$$

$$\langle n_i' n_j' \rangle_{av} = \bar{n}_i' \bar{n}_j',$$

then

$$a_i^k = a_k^i \exp[\beta(\epsilon_i - \epsilon_k)]. \quad (3.6)$$

Proof: Since the proof for (i) is a special case of that for (ii), consider case (ii). We can write (3.5) as

$$a_i^k = \sum_{j,l} A_{ij}^{kl} [\bar{n}_j' (1 + \theta' \bar{n}_l')] \\ = \sum_{j,l} A_{ij}^{kl} \{ [\bar{n}_j' / (1 + \theta' \bar{n}_j')] [(1 + \theta' \bar{n}_l') / \bar{n}_l'] \} \\ \times \bar{n}_l' (1 + \theta' \bar{n}_j').$$

In virtue of (ii), the factor in curly brackets is $\exp\beta(\epsilon_l - \epsilon_j)$ and, hence, depends only on the energy transfer and not on the individual energies of the colliding particles. But from the conservation of energy in the transition $(i,j) \rightarrow (k,l)$, it follows that $\epsilon_l - \epsilon_j = \epsilon_i - \epsilon_k$; i.e., the quantity in square brackets is independent of j and l . It may therefore be factored outside the sum so that

$$a_i^k = [\exp\beta(\epsilon_i - \epsilon_k)] \sum_{j,l} A_{ij}^{kl} \bar{n}_l' (1 + \theta' \bar{n}_j') \\ = [\exp\beta(\epsilon_i - \epsilon_k)] \sum_{j,l} A_{kl}^{ij} \bar{n}_l' (1 + \theta' \bar{n}_j') \\ = a_k^i \exp\beta(\epsilon_i - \epsilon_k).$$

In the second step microscopic reversibility, $A_{ij}^{kl} = A_{kl}^{ij}$, has been assumed. The basic property (3.6) of the a_i^k is quite general. The validity of the proof is not restricted by the assumption of binary collisions; and, in fact, a completely analogous proof can be given which includes all higher order collisions as well as the possibility of emission and absorption.²⁸

2. Rate Equations

Rate equations for the relaxing system are easily obtained from (3.4) by using (2.9). Thus for the mean values of the occupation numbers one gets

$$d\bar{n}_k/dt = \sum_i \{ a_i^k [\bar{n}_i + \theta \langle n_i n_k \rangle_{av}] - a_k^i [\bar{n}_k + \theta \langle n_i n_k \rangle_{av}] \}. \quad (3.7)$$

This set of equations is only a partial characterization of the relaxation; additional equations are required to determine $\langle n_i n_k(t) \rangle_{av}$. If the occupation numbers are uncorrelated the set of equations (3.7) is closed but nonlinear. However, if the relaxing system consists of M. B. particles, (3.7) reduces to

$$d\bar{n}_k/dt = \sum_i (a_i^k \bar{n}_i - a_k^i \bar{n}_k) = \sum_i \Lambda_{ik} \bar{n}_i, \quad (3.8)$$

where

$$\Lambda_{ik} = a_i^k - \delta_i^k \sum_j a_i^j. \quad (3.9)$$

(δ_i^k is the Kronecker delta.)

This is a system of linear differential equations with the formal solution

$$\langle \bar{n}(t) | = \langle \bar{n}(0) | T(t), \quad (3.10)$$

where $\bar{n}_k(t)$, $k=0, 1, 2, \dots$, are the components of the row vector $\langle \bar{n}_k(t) |$, and the square matrix $T(t)$ is that solution of the matrix equation

$$dT/dt = T\Lambda, \quad (3.11)$$

which satisfies the initial condition

$$T_{ij}(0) = \delta_i^j. \quad (3.12)$$

When Λ is finite dimensional there exists a unique matrix $T(t)$ which satisfies (3.11) and (3.12), namely

$$T(t) = e^{\Lambda t}. \quad (3.13)$$

When Λ is an infinite dimensional matrix, there are cases²⁹ in which there can be more than one solution $T(t)$ satisfying (3.11) and (3.12). We shall assume that for any Λ of physical interest the matrix $T(t)$ defined

²⁸ Although the property (3.6) is well known, the usual proofs entail more restrictive assumptions. See, for example, M. J. Klein and P. H. E. Meijer, Phys. Rev. **96**, 250 (1954); C. Kittel, *Elementary Statistical Physics* (John Wiley & Sons, Inc., New York, 1958), Sec. 39; J. H. Van Vleck, Suppl. Nuovo cimento **6**, 1081 (1957). Our proof is a generalization of one given by R. T. Cox, Revs. Modern Phys. **22**, 238 (1950). Cox adopts the point of view of Gibbs in that he takes the index i to refer to the state of a whole macroscopic system rather than to an individual particle state as we do (following Boltzmann). The relation of the form (3.6) which he obtains applies to two states i and j of subsystems of a canonical ensemble.

²⁹ See Appendix I and the references cited there.

by (3.11) and (3.12) is unique and has a unique spectral representation

$$T(t) = \sum_k e^{\lambda_k t} |x(k)\rangle\langle y(k)|, \quad (3.14)$$

where λ_k , $k=0, 1, 2, \dots$, are eigenvalues of Λ , and $|x(k)\rangle$ and $\langle y(k)|$ are the corresponding column and row eigenvectors which satisfy the completeness and orthogonality relations

$$\sum_k |x(k)\rangle\langle y(k)| = I, \quad (3.15)$$

and

$$\langle y(k)|x(l)\rangle = \delta_{kl}, \quad (3.16)$$

where I is the unit matrix.

Explicit determination of the eigenvalues λ_k and the eigenvectors $|x(k)\rangle$ and $\langle y(k)|$ is usually not simple. However, for the case of interacting harmonic oscillators, considered in the next section, Montroll and Shuler¹⁸ obtained the solution to (3.8) by a generating function method. We shall extract from this solution the eigenvalues and eigenvectors appropriate to that problem. (See Appendix II.)

B. General Solution for M.B. Particles

We now turn to the problem of exhibiting an explicit solution to Eq. (3.4). When $\theta = \mp 1$, corresponding to F.D. and B.E. particles, Eq. (3.4) is a second order partial differential equation which we have been unable to solve. However, for $\theta = 0$, the case of classical M.B. particles, the equation reduces to

$$\frac{\partial \Phi}{\partial t} = \sum_{i,k} a_{ik} (z_k - z_i) \frac{\partial \Phi}{\partial z_i} = \sum_{i,k} \Lambda_{ik} z_k \frac{\partial \Phi}{\partial z_i}, \quad (3.17)$$

which, being a first order partial differential equation, can be solved by the method of characteristics.³⁰ The differential equations for the characteristics are

$$dt = -dz_i / \sum_j \Lambda_{ij} z_j, \quad i=0, 1, 2, \dots, \quad (3.18)$$

or, in matrix form,

$$d|z\rangle/dt = -\Lambda|z\rangle. \quad (3.19)$$

The solution of this equation is

$$T(t)|z\rangle = \text{constant vector}. \quad (3.20)$$

Changing the independent variables in (3.17) to t and $|\eta\rangle$ where

$$|\eta\rangle = T(t)|z\rangle, \quad (3.21)$$

we may write the solution for $\Phi(|z\rangle; t)$ of (3.17) as

$$\Phi(|z\rangle; t) = f(|\eta\rangle),$$

where f is an arbitrary function of the $|\eta\rangle$ which, however, is uniquely determinable once the initial conditions are specified. These conditions may, for

example, be the number of particles n_i^0 in each state i at $t=0$. More generally we shall suppose that $P(\langle n|; 0)$ at $t=0$ is given.³¹ Thus let

$$\Phi(|z\rangle; 0) \equiv \Phi_0(|z\rangle) \quad (3.22)$$

be the initial PGF. Then from (3.20) and (3.21), we have

$$\Phi_0(|z\rangle) = f(|z\rangle),$$

and hence,

$$\begin{aligned} \Phi(|z\rangle; t) &= f(|\eta\rangle) = \Phi_0(|\eta\rangle) \\ &= \Phi_0(T(t)|z\rangle). \end{aligned} \quad (3.23)$$

Equations (3.23) and (3.10) show that the time dependent behavior of both the JPD of the occupation numbers and the mean values of the occupation numbers is determined by the same matrix $T(t) = e^{\Lambda t}$. In particular, it follows that if one knows the mean values of the occupation numbers $\bar{n}_i(t)$ for all time and for an arbitrary set of initial values, then this is sufficient to determine $P(\langle n|; t)$ and, hence, all higher moments $\langle n_i^2(t) \rangle_{av}$, $\langle n_i n_j(t) \rangle_{av}$, etc., for all time.

1. The Stationary Solution

We now consider the stationary, i.e., time independent, solutions of (3.8) and (3.17). In particular, we show how to construct the solution of one from that of the other. First we list several known properties³² of the stochastic matrix $T(t)$:

- (i) $T_{ij}(t) \geq 0$;
- (ii) $\sum_j T_{ij}(t) = 1$;
- (iii) The limit, $T(\infty) \equiv \lim_{t \rightarrow \infty} T(t)$ exists, or equivalently, there is at least one λ_k equal to zero in the spectral representation (3.14). All the nonzero λ_k have negative real parts. [That Λ has in fact at least one zero eigenvalue, say λ_0 , follows from $\sum_j \Lambda_{ij} = 0$ which implies that the column vector $|x(0)\rangle$ with all components equal:

$$x_i(0) = 1, \quad i=1, 2, \dots, \quad (3.24)$$

is a right eigenvector belonging to $\lambda_0 = 0$.]

We shall assume, in addition:

- (iv) The relaxing system is ergodic, i.e., that for every pair of states i, k there exists a sequence of states j_1, j_2, \dots, j_r such that $\Lambda_{ij_1} \Lambda_{j_1 j_2} \dots \Lambda_{j_r k}$ is nonzero. (Physically, ergodicity means that every state is accessible from every other.) The limit $T_{ij}(\infty)$ is then independent of i . This is equivalent to the non-degeneracy of the zero eigenvalue in the spectral representation (3.14). Indeed, using this fact and (iii), one gets

$$\lim_{t \rightarrow \infty} T(t) = |x(0)\rangle\langle y(0)|, \quad (3.25)$$

³¹ Specifying the number of particles in each state at $t=0$ corresponds to choosing the particular initial distribution $P(\langle n|; 0) = \Pi_i \delta(n_i, n_i^0)$.

³² M. Fréchet, *Recherches Théoriques Modernes sur le Calcul des Probabilités* (Gauthier-Villars, Paris, 1952).

³⁰ See, for example, R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Verlag Julius Springer, Berlin, 1927), Vol. II. Also, M. S. Bartlett, J. Roy. Stat. Soc. B11, 211 (1949).

so that by (3.24)

$$T_{ij}(\infty) = y_j(0). \quad (3.26)$$

Finally, we shall use the fact:

(v) $T(\infty)$ is a stationary solution of (3.11). In fact, if $F(t)$ is a solution of a differential equation which is of the first order in time, such as (3.8), (3.17), or (2.5), then if $F(\infty) \equiv \lim_{t \rightarrow \infty} F(t)$ exists it is a stationary solution F_s , [i.e., $F_s(t) = F_s(t+\tau)$ for all t], and conversely. Hence, we may obtain the unique stationary solution as the $\lim_{t \rightarrow \infty} F(t)$ when this latter exists: $F_s = F(\infty)$.

We can now completely characterize the stationary solutions of (3.8) and (3.17): *The stationary solutions $\langle \bar{n}_s \rangle$ and $P_s(\langle n \rangle)$ [or $\Phi_s(|z\rangle)$] are unique, independent of initial conditions, and depend only on the row eigenvector $\langle y(0) |$ of Λ . If N is the total number of particles in the relaxing system, and $\langle \bar{n}(t) |$ and $P(\langle n |; t)$ are any solutions for the mean values of the occupation numbers and for the JPD respectively, then*

$$\langle \bar{n}_s \rangle = \lim_{t \rightarrow \infty} \langle \bar{n}(t) | = N \langle y(0) |, \quad (3.27)$$

where $\langle y(0) |$ is the row eigenvector of Λ belonging to $\lambda_0 = 0$; and

$$\begin{aligned} P_s(\langle n \rangle) &= \lim_{t \rightarrow \infty} P(\langle n |; t) \\ &= \frac{N!}{\prod_i n_i!} \prod_i [y_i(0)]^{n_i} \\ &= \frac{N!}{\prod_i n_i!} \prod_i \left[\frac{\bar{n}_i(\infty)}{N} \right]^{n_i}, \quad \sum_i n_i = N. \end{aligned} \quad (3.28)$$

The associated PGF is given by

$$\Phi_s(|z\rangle) = \langle y(0) | z \rangle^N. \quad (3.29)$$

These equations follow directly on using (v), (3.24), and (3.25). Thus,

$$\begin{aligned} \langle \bar{n}(\infty) | &= \lim_{t \rightarrow \infty} \langle \bar{n}(0) | T(t) \\ &= \langle \bar{n}(0) | x(0) \rangle \langle y(0) | \\ &= N \langle y(0) |, \end{aligned} \quad (3.30)$$

and

$$\begin{aligned} \Phi(|z\rangle; \infty) &= \lim_{t \rightarrow \infty} \Phi_0(T(t)|z\rangle) \\ &= \Phi_0(|x(0)\rangle \langle y(0)|z\rangle) \\ &= \sum_{\langle n |} P(\langle n |; 0) \prod_i \langle y(0) | z \rangle^{n_i} \\ &= \langle y(0) | z \rangle^N \sum_{\langle n |} P(\langle n |; 0) \\ &= \langle y(0) | z \rangle^N. \end{aligned} \quad (3.31)$$

Equation (3.28) for $P_s(\langle n |)$ then follows from (3.31) by using the multinomial expansion.

From Eq. (3.31) one can readily obtain all desired moments and marginal distributions of the stationary JPD (3.28). For example, $\Phi(z_i; \infty)$, the marginal PGF, is obtained by setting all z 's, except z_i , equal to unity in (3.31). Thus, in virtue of (3.16) and (3.24), we find

$$\Phi(z_i; \infty) = [1 - (1 - z_i)y_i(0)]^N. \quad (3.32)$$

The corresponding stationary marginal probability distribution of n_i is then readily seen to be

$$P(n_i; \infty) = \binom{N}{n_i} \left(\frac{\bar{n}_i}{N} \right)^{n_i} \left(1 - \frac{\bar{n}_i}{N} \right)^{N-n_i}, \quad (3.33)$$

which is a binomial distribution with mean \bar{n}_i and relative variance

$$\frac{\langle n_i^2(\infty) \rangle_{av} - \bar{n}_i^2(\infty)}{\bar{n}_i^2(\infty)} = \left(\frac{1}{\bar{n}_i} - \frac{1}{N} \right). \quad (3.34)$$

Similarly, the marginal PGF for the joint occupation number distribution for any two states i and j is

$$\Phi(z_i, z_j; \infty) = [1 - (1 - z_i)y_i(0) - (1 - z_j)y_j(0)]^N, \quad (3.35)$$

from which it follows that

$$P(n_i, n_j; \infty) = \frac{N!}{n_i! n_j! n_k!} \left(\frac{\bar{n}_i}{N} \right)^{n_i} \left(\frac{\bar{n}_j}{N} \right)^{n_j} \left(\frac{\bar{n}_k}{N} \right)^{n_k}, \quad (3.36)$$

where

$$n_k = N - (n_i + n_j).$$

The correlation coefficient of these occupation numbers is given by

$$\frac{\langle n_i(\infty) n_j(\infty) \rangle_{av} - \bar{n}_i(\infty) \bar{n}_j(\infty)}{\bar{n}_i(\infty) \bar{n}_j(\infty)} = \frac{1}{N}, \quad i \neq j. \quad (3.37)$$

Generally, for the average of the product of the occupation numbers for r states i_1, i_2, \dots, i_r , one gets

$$\langle n_{i_1}(\infty) \dots n_{i_r}(\infty) \rangle_{av} = \frac{N!}{(N-r)!} \prod_{i=1}^r \left(\frac{\bar{n}_{i_j}(\infty)}{N} \right), \quad (3.38)$$

where all the i_j are distinct.

We now state certain obvious consequences of the preceding development which are of interest inasmuch as they extend the familiar results of statistical mechanics for systems in thermal equilibrium to the stationary distribution of an ergodic system interacting with any stationary (not necessarily thermal) reservoir. (For the case of a thermal reservoir, see below.)

(i) The stationary JPD given by Eq. (3.28) is *not* a product of independent distributions for each state. This is due to the constraint $\sum n_i = N$ which induces a weak but nonvanishing negative correlation in the occupation numbers. [See Eq. (3.37).]

(ii) The stationary JPD is expressible wholly in terms of the average occupation numbers $\bar{n}_i(\infty)$.

(iii) For N sufficiently large and $\bar{n}_i \ll N$, we find that $P(n_i; \infty)$, given by Eq. (3.33), approaches a Poisson distribution

$$P(n_i; \infty) = e^{-\bar{n}_i} \bar{n}_i^{n_i} / n_i! \quad (3.39)$$

where $\bar{n}_i \equiv \bar{n}_i(\infty)$.

(iv) The formulas of this section all reduce to those for a canonical ensemble at the temperature $T = 1/(k\beta)$ when the $\bar{n}_i(\infty)$ are given by the Maxwell-Boltzmann values

$$\bar{n}_i = N e^{-\beta \epsilon_i} / \sum_j e^{-\beta \epsilon_j} \quad (3.40)$$

(v) The mean occupation numbers $\bar{n}_i(\infty)$ for the general stationary solution of the rate equation (3.8) do not satisfy the detailed balance condition

$$a_i^k \bar{n}_i(\infty) = a_k^i \bar{n}_k(\infty), \quad \text{all } i, k. \quad (3.41)$$

For this condition to be satisfied the a_i^k must satisfy the consistency relations

$$a_i^k a_k^l a_l^i = a_i^l a_l^k a_k^i, \quad i \neq l \neq k \neq i. \quad (3.42)$$

(vi) The form of the stationary JPD (3.28) is a multinomial distribution in the occupation numbers. This form has the remarkable property that *if the initial JPD has this form, then the JPD will preserve this form for all time* with the mean occupation numbers, $\bar{n}_i(t)$, being given by the solution (3.10) of the rate equation (3.8) for the given initial means $\bar{n}_i(0)$. This conclusion follows readily from (3.29) and (3.23):

$$\begin{aligned} \Phi(|z\rangle; t) &= \Phi_0(T(t)|z\rangle) = (1/N^N) \langle \bar{n}(0) | T(t) | z \rangle^N \\ &= (1/N^N) \langle \bar{n}(t) | z \rangle^N. \end{aligned}$$

2. Stationary Solution with Thermal Reservoir

Let us now assume that the relaxing set interacts with a thermal reservoir at the temperature T . Since the form of the JPD is given by (3.28), it remains only to determine the unique set of $\bar{n}_i(\infty)$ appropriate to this case. We do this by noting that in virtue of (3.6), the a_i^k for the case of a thermal reservoir do satisfy the consistency relations (3.42). Hence, a possible solution of the rate equation (3.8) is that for which the $\bar{n}_i(\infty)$ satisfy the detailed balance relation (3.41). From this and (3.6) one gets the M.B. average occupation numbers (3.40). From the discussion of the preceding subsection, it follows that this solution is unique and corresponds to the canonical ensemble.³³

It was, of course, to be expected that a system interacting with a thermal reservoir would approach a thermal distribution at the reservoir temperature. However, in Sec. IV we give an example showing that it is possible for the relaxing system to approach thermal equilibrium even when the reservoir is not thermal.

³³ For a different proof, see Siegert, reference 15.

3. Time Dependent Correlations and Fluctuations

We now return to the general time dependent solution $\Phi(|z\rangle; t)$ of (3.17) and extract from it the time dependent correlations and fluctuations in the occupation numbers. To obtain these in terms of their initial values at $t=0$, we apply (2.9) to the solution (3.23) for the PGF in the form $\Phi_0(|\eta\rangle)$. Then Φ_0 incorporates the initial conditions and $|\eta\rangle \equiv T(t)|z\rangle$ incorporates the time dependence. The following relations are now useful:

$$d\eta_i/dz_j = T_{ij}(t), \quad (3.43)$$

and

$$|\eta\rangle = |x(0)\rangle \quad \text{when all } z_j = 1, \quad (3.44)$$

i.e., $\eta_i = 1$ for all i when all $z_j = 1$. The first relation follows immediately from (3.21) while the latter follows from the additional fact that $\sum_j T_{ij}(t) = 1$. Using these relations, one readily finds the correlations of the occupation numbers:

$$\begin{aligned} \langle n_i(t) n_j(t) \rangle_{av} &= \sum_k T_{ki} [(\delta_i^j - T_{kj}) \bar{n}_k(0) \\ &\quad + \sum_l T_{lj} \langle n_k n_l(0) \rangle_{av}]. \end{aligned} \quad (3.45)$$

In a similar manner one can obtain the time dependence of all other higher moments, correlations, and fluctuations in the occupation numbers.

In the limit $t \rightarrow \infty$, we find³⁴

$$T_{ki} \rightarrow x_k(0) y_i(0) = y_i(0) = \bar{n}_i(\infty) / N, \quad (3.46)$$

and we easily recover from (3.45) the results for the variance and covariance obtained earlier for the stationary distribution.

It is noteworthy that, unlike the stationary solutions, the JPD at any finite time in general cannot be specified solely in terms of the mean occupation numbers at that time.

IV. RELAXING SET OF HARMONIC OSCILLATORS

We now consider in detail an example of a relaxing system in interaction with a reservoir. We suppose that both the system and the reservoir consist of identical harmonic oscillators (e.g., the vibrational modes of identical diatomic molecules). The major portion of these (the reservoir) is prepared and maintained with a stationary occupation number distribution, while the remaining N relaxing oscillators may have an arbitrary distribution.

Relaxation takes place through collision with the reservoir oscillators. It is assumed, following Landau and Teller,³⁵ that the interaction energy of two colliding oscillators depends linearly on the vibrational coordinate of each of them. This interaction is effective during the "collision time" and causes simultaneous changes in the states of the two oscillators. The transi-

³⁴ Note that the argument of $|x\rangle$ or $\langle y|$ is the eigenvalue to which the eigenvector belongs, whereas time is the argument of the occupation numbers n_i .

³⁵ L. Landau and E. Teller, *Physik. Z. Sowjetunion* **10**, 34 (1936).

tion probabilities per collision, $(i, j) \rightarrow (k, l)$, as obtained from first order quantum mechanical perturbation theory, are³⁶

$$\begin{aligned} A_{ij}^{kl} &= 0 \quad \text{unless } k=i\pm 1 \text{ and } l=j\mp 1, \\ A_{ij}^{i+1, j-1} &= C(i+1)j, \\ A_{ij}^{i-1, j+1} &= Ci(j+1), \end{aligned} \quad (4.1)$$

where the positive constant C is a measure of the coupling strength between the oscillators. (For a discussion of the application of this model to chemical kinetics and the relaxation of vibrationally excited gases, see references 17-19.)

It follows from (3.5) (with $\theta=0$) and (4.1) that

$$\begin{aligned} a_i^k &= 0 \quad \text{unless } k=i\pm 1, \\ a_{i+1}^i &= C(i+1) \sum_{j=0}^{\infty} (j+1) \bar{n}_j', \\ a_i^{i+1} &= C(i+1) \sum_{j=0}^{\infty} j \bar{n}_j', \end{aligned} \quad (4.2)$$

where the \bar{n}_j' are the mean occupation numbers for the (not necessarily thermal) reservoir.

For oscillators with frequency ν , the energy levels are $\epsilon_i = (i + \frac{1}{2})h\nu$, and the average energy of a reservoir oscillator is (in units of $h\nu$)

$$\bar{\epsilon} = \sum_j (j + \frac{1}{2}) \bar{n}_j' / \sum_j \bar{n}_j'. \quad (4.3)$$

Defining

$$\epsilon_{\pm} = \bar{\epsilon} \pm \frac{1}{2}, \quad (4.3)$$

we may write

$$\frac{a_i^{i+1}}{a_{i+1}^i} = \frac{(\bar{\epsilon} - \frac{1}{2})}{(\bar{\epsilon} + \frac{1}{2})} = \frac{\epsilon_-}{\epsilon_+}. \quad (4.4)$$

This ratio depends only on the average energy per particle of the reservoir. In particular, it is independent of the state i . If the reservoir is thermal (4.4) reduces to (3.6). Note also that

$$a_{i+1}^i - a_i^{i+1} = C(i+1) \sum_j \bar{n}_j' = c(i+1), \quad (4.5)$$

where $c = C \sum_j \bar{n}_j'$.

Thus, for this model the a_i^j , and hence the entire probabilistic description of the relaxation process, depend only on the two physical parameters c and $\bar{\epsilon}$.

³⁶ This expression for the transition probability per collision is correct only so long as $Cij \ll 1$, since its derivation tacitly assumes that, during the effective interaction time, each of the oscillators participating in a collision undergoes only one transition (or none at all). The expression is no longer valid for collisions between oscillators in very high energy states (i, j large) because there is then a finite probability for the occurrence of several transitions during the course of one collision. This would leave the oscillators in final states whose quantum numbers, in general, would differ from those of the initial states by more than one, contrary to our assumption. We shall avoid this difficulty by confining our attention to systems in which the populations of such high energy states are negligibly small. Hence, while continuing to use the same expression for the transition probability, we shall refrain from interpreting Cij as a transition probability per collision when ij is large.

In terms of these the Λ matrix can be written as

$$\Lambda = c \begin{pmatrix} -\epsilon_- & \epsilon_- & 0 & 0 & \cdots \\ \epsilon_+ & -(\epsilon_+ + 2\epsilon_-) & 2\epsilon_- & 0 & \cdots \\ 0 & 2\epsilon_+ & -(2\epsilon_+ + 3\epsilon_-) & 3\epsilon_- & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (4.6)$$

The problem now is to use this Λ matrix to determine $\langle \bar{n}(t) |$, the solution to the rate equation (3.8). Then the solution (3.23) for $\Phi(|z\rangle; t)$ will also be determined. Montroll and Shuler¹⁸ obtained $\langle \bar{n}(t) |$ by solving for the generating function $G(u; t)$ defined by Eq. (A II.5). They were not concerned with, and therefore did not obtain, the matrix elements $T_{ij}(t)$, or the eigenvalues and eigenvectors of the matrix Λ which are needed to determine the time dependent correlations in the occupation numbers. [See Eqs. (3.45) and (3.14).] In Appendix II, we shall obtain the eigenvalues and eigenvectors for a slightly more general matrix than (4.6). On specializing that result to the present case, we find that the double generating function

$$G(u, v; t) = \sum_{i, j=0}^{\infty} T_{ij}(t) v^i u^j \quad (4.7)$$

of $T_{ij}(t)$ is given by

$$G(u, v; t) = \{ [(\epsilon_+ - u\epsilon_-) - \epsilon_- (1-u)e^{-ct}] - v[(\epsilon_+ - u\epsilon_-) - \epsilon_+ (1-u)e^{-ct}] \}^{-1}. \quad (4.8)$$

Expansion of (4.8) leads to the two alternative expressions

$$T_{ij}(t) = [\epsilon_+ (1 - e^{-ct})]^{i-j} [\epsilon_- - \epsilon_+ e^{-ct}]^j \times [\epsilon_+ - \epsilon_- e^{-ct}]^{-i-1} {}_2F_1(-j, i+1; 1; s), \quad (4.9a)$$

or

$$T_{ij}(t) = [\epsilon_- (1 - e^{-ct})]^{j-i} [\epsilon_- - \epsilon_+ e^{-ct}]^i \times [\epsilon_+ - \epsilon_- e^{-ct}]^{-i-1} {}_2F_1(-i, j+1; 1; s), \quad (4.9b)$$

where

$$s = e^{-ct} [(\epsilon_+ - \epsilon_- e^{-ct})(\epsilon_+ e^{-ct} - \epsilon_-)]^{-1}, \quad (4.10)$$

and the ${}_2F_1$ are hypergeometric functions simply related to the Jacobi polynomials. The identity³⁷

$$\begin{aligned} (1-w)^{a-1} (1-w+sw)^{-a} \\ = \sum_{n=0}^{\infty} w^n {}_2F_1(-n, a; 1; s); \\ |w| < 1, \quad |w(1-s)| < 1, \end{aligned} \quad (4.11)$$

has been used in obtaining the above expressions.

In the present case, the eigenvalues λ_k in the spectral representation (3.14) of $T(t)$ are (see Appendix II):

$$\lambda_k = -kc, \quad k=0, 1, 2, \dots \quad (4.12)$$

³⁷ See, for example, A. Erdelyi *et al.*, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 82.

The corresponding row and column eigenvectors have the respective generating functions

$$G_R(u, k) \equiv \sum_i y_i(k) u^i = \epsilon_-^k (1-u)^k (\epsilon_+ - \epsilon_- u)^{-k-1}, \quad (4.13)$$

and

$$G_C(v, k) \equiv \sum_i x_i(k) v^i = \epsilon_-^{-k} (1-v)^{-k-1} (\epsilon_- - \epsilon_+ v)^k. \quad (4.14)$$

These equations, in conjunction with (3.14) and (3.23), give the time dependent JPD in the occupation numbers explicitly for the system under consideration. We now examine several properties of our solution which are specific to this model.

Consider first the stationary JPD $P(\langle n |; \infty)$ given by (3.28). To determine this JPD, one needs the $\bar{n}_i(\infty) = N y_i(0)$. From (4.13), one gets

$$\begin{aligned} y_i(0) &= \epsilon_+^{-1} (\epsilon_- / \epsilon_+)^i \\ &= \frac{(\epsilon_- / \epsilon_+)^{i+\frac{1}{2}}}{\sum_{j=0}^{\infty} (\epsilon_- / \epsilon_+)^{j+\frac{1}{2}}}. \end{aligned} \quad (4.15)$$

Let us now introduce a parameter T defined by the relation³⁸

$$T = (1/k) \ln(\epsilon_+ / \epsilon_-). \quad (4.16)$$

Then the average occupation numbers for the stationary distribution of the relaxing oscillators are given by

$$\bar{n}_i(\infty) = N \frac{\exp[-(i+\frac{1}{2})/kT]}{\sum_j \exp[-(j+\frac{1}{2})/kT]}. \quad (4.17)$$

These are precisely the Maxwell-Boltzmann values of the $\bar{n}_i(\infty)$ [see (3.40)] for a system of harmonic oscillators of frequency ν in thermal equilibrium at the temperature T .³⁹ Thus, the stationary JPD of the occupation numbers of the relaxing set of harmonic oscillators is the same as that for a canonical ensemble corresponding to thermal equilibrium at a temperature T defined by (4.16) *irrespective of the reservoir distribution*. The equilibrium temperature T of the relaxing system is determined only by the average energy per reservoir particle. The reservoir itself need not be in thermal equilibrium!

One can give another formal argument why the stationary values of the average occupation numbers should correspond to a thermal distribution for the case of interacting oscillators considered here. Namely, in Sec. III.B.2, it was seen that if the a_i^j satisfy (3.6) the $\bar{n}_i(\infty)$ for the relaxing set will be Maxwellian. But in virtue of (4.2), (4.4), and the definition (4.16), the relation (3.6) is satisfied for this system irrespective of

the specification of the average occupation numbers \bar{n}_i' of the reservoir. One may readily verify that this striking result would no longer be true if the interaction energy between harmonic oscillators were taken as proportional to the cube of each oscillator coordinate rather than linear in it, or if the energy levels of the interacting system were discrete but had at least one spacing incommensurable with the others.

For most initial conditions the explicit expression for $\Phi(|z|; t)$ is not particularly perspicuous. However, there is one important exception which we now consider. Let the initial distribution of the relaxing system be thermal at a temperature $T_0 \neq T$, where T is defined by (4.16). Then the initial PGF is

$$\Phi_0(|z|) = [\sum_j e^{-i\beta_0} (1 - e^{-\beta_0}) z_j]^N. \quad (4.18)$$

A simple computation based on (3.10) and (3.23) then shows that at any later time

$$\Phi(|z|; t) = [\sum_j e^{-i\beta(t)} (1 - e^{-\beta(t)}) z_j]^N, \quad (4.19)$$

where

$$\beta(t) = \ln \left(\frac{e^{-\epsilon t} (1 - e^{\beta_\infty - \beta_0}) - e^{\beta_\infty} (1 - e^{-\beta_0})}{e^{-\epsilon t} (1 - e^{\beta_\infty - \beta_0}) - (1 - e^{-\beta_0})} \right), \quad (4.20)$$

$\beta_0 = 1/(kT_0)$, and $\beta_\infty = 1/(kT)$. [By differentiating (4.20), one can easily show that $\beta(t)$ is a monotonic function of t .] This establishes that *if the JPD of the occupation numbers is initially thermal it remains thermal with a temperature $T(t)$ which varies monotonically with time from the given initial T_0 to a final value T at $t = \infty$ determined by the reservoir* [see (4.16)]. This is not surprising in view of the corresponding result for the mean values of the occupation numbers obtained by Montroll and Shuler¹⁸ for this model, and the general property, mentioned in remark (vi) of Sec. III.B.1, that the multinomial JPD preserves its form for all time.

Another interesting aspect of the approach to equilibrium, which was noted by Montroll and Shuler,¹⁸ is that the mean energy content $\bar{E}(t)$ of the relaxing system approaches its equilibrium value exponentially. This result follows directly on using the eigenvalues and eigenvectors of Λ . Thus, using (3.10), we see that

$$\bar{E}(t) = \sum_j (j + \frac{1}{2}) \bar{n}_j(t) = \sum_{i,j} (j + \frac{1}{2}) T_{ij} \bar{n}_i(0), \quad (4.21)$$

and noting that $\sum_j j T_{ij}(t)$ is the coefficient of v^i in the expansion of $[\partial G(u, v; t) / \partial u]_{u=1}$ we obtain

$$\bar{E}(t) = [\bar{E}(0) - N\bar{\epsilon}] e^{-\epsilon t} + N\bar{\epsilon}. \quad (4.22)$$

Hence,

$$\bar{E}(\infty) = N\bar{\epsilon}, \quad (4.23)$$

and

$$\bar{E}(t) - \bar{E}(\infty) = [\bar{E}(0) - \bar{E}(\infty)] e^{-\epsilon t}, \quad (4.24)$$

which shows that the average energy of the relaxing system at any time depends only on the average energy at $t=0$ and not on how it was distributed initially among the various states. We can, using our more

³⁸ In particular, if the reservoir is thermal at a temperature T_R , then (4.3) yields the familiar average energy per oscillator $\bar{\epsilon} = \frac{1}{2} \coth(1/2kT_R)$, and (4.16) yields $T = T_R$.

³⁹ Note that all energies are expressed in units of $h\nu$.

general method, obtain a similar result for the variance of the energy. Thus,

$$\begin{aligned}\sigma_E^2(t) &= \langle E^2(t) \rangle_{av} - \bar{E}^2(t) \\ &= \sum_{i,j} (i + \frac{1}{2})(j + \frac{1}{2}) \sum_k \{ \bar{n}_k(0) [T_{ki} \delta_{ij} - T_{ki} T_{kj}] \\ &\quad + \sum_l [\langle n_k n_l(0) \rangle_{av} - \bar{n}_k(0) \bar{n}_l(0)] T_{li} T_{lj} \}. \quad (4.25)\end{aligned}$$

Using the generating function $G(u, v; t)$ as before, we obtain, after some calculation

$$\frac{[\sigma_E^2(t) - \sigma_E^2(\infty)] - \bar{E}[\bar{E}(t) - \bar{E}(\infty)]}{[\sigma_E^2(0) - \sigma_E^2(\infty)] - \bar{E}[\bar{E}(0) - \bar{E}(\infty)]} = e^{-2ct}. \quad (4.26)$$

V. RELAXATION INCLUDING NONCONSERVATION OF PARTICLES

In the example treated in Sec. IV, the number of harmonic oscillators remained constant throughout the relaxation process.

In this section we consider a generalization of this model, allowing for the possibilities that during the relaxation process

(1) Harmonic oscillators appear in the various states i at a rate which is a function only of i (and not of n_i), and

(2) Harmonic oscillators disappear from the various states i at a rate which is a function of i and n_i .

The first possibility arises when a chemical reaction is taking place which produces harmonic oscillators in various states at varying rates. The second occurs in practice due to the dissociation of the harmonic oscillators (or, rather, of the diatomic molecules) which are in states with energy greater than the dissociation energy.⁴⁰

The determination of the JPD in these cases, as in the simpler case treated in the last section, is intimately related to the solution of the equations for the average occupation numbers \bar{n}_i . It has not been possible to solve these equations explicitly with a completely realistic energy dependence for the dissociation rate, but the explicit solution can be obtained if this rate increases linearly with energy. We present this derivation below, since it gives a further illustration of the method outlined in the last section; it may also be expected that the solution exhibits the main features of the actual problem with dissociation.

We make the following definitions:

(1) ν_i = probability per unit time that in the relaxing subsystem a new oscillator is created in the state i , and

(2) $n_i \mu_i$ = probability per unit time that an oscillator disappears (through "dissociation") from state i , given that the occupation number of this state is n_i .

The equation for the JPD of the occupation numbers now follows from (2.5) when the appropriate Q is

⁴⁰ Related problems have been considered by E. W. Montroll and K. Shuler, *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1958), Vol. I; and F. Buff and D. Wilson, *J. Chem. Phys.* **32**, 677 (1960).

introduced. We readily find

$$\begin{aligned}\frac{\partial P(\langle n \rangle; t)}{\partial t} &= \sum_{\langle m \rangle} P(\langle m \rangle; t) Q_I(\langle m \rangle \rightarrow \langle n \rangle) \\ &\quad + \sum_i [- (\nu_i + n_i \mu_i) P(\langle n \rangle; t) \\ &\quad + \nu_i P(n_1, n_2, \dots, n_i - 1, \dots; t) \\ &\quad + \mu_i P(n_1, n_2, \dots, n_i + 1, \dots; t)]. \quad (5.1)\end{aligned}$$

Here Q_I is that part of Q which refers to collisions between particles of the relaxing system and those of the reservoir. In the equation for the generating function Φ , it leads to a term identical with the right side of (3.4) (with $\theta=0$). We thus have

$$\begin{aligned}\frac{\partial \Phi(z; t)}{\partial t} &= \sum_i \left[- \sum_j a_i^j (z_i - z_j) \frac{\partial}{\partial z_j} \right. \\ &\quad \left. + (z_i - 1) \left(\nu_i - \mu_i \frac{\partial}{\partial z_i} \right) \right] \Phi. \quad (5.2)\end{aligned}$$

It must be noted that the operator acting on the right side of (5.2) is not of the form obtained by replacing n by $z(\partial/\partial z)$ in (2.17). The reason is that the Q of the present case has a part that depends on ν and hence represents the production of particles by an external agency (independent of the occupation numbers). This part is not of the form (2.16) on which (2.17) is based.

If we now set $z_i - 1 = w_i$, Eq. (5.2) becomes

$$\frac{\partial \Phi}{\partial t} = \sum_i \left[\sum_j L_{ij} w_j \frac{\partial \Phi}{\partial w_i} + \nu_i w_i \Phi \right], \quad (5.3)$$

where

$$L_{ij} = a_i^j - \delta_{ij} (\sum_k a_i^k + \mu_i). \quad (5.4)$$

(The symbol Φ is retained for convenience.)

Note that the mean values of the occupation numbers obey the equation

$$(\partial/\partial t) \langle \bar{n}(t) \rangle = \langle \bar{n} | L + \nu |, \quad (5.5)$$

with the formal solution

$$\langle \bar{n}(t) \rangle = \langle \bar{n}(0) | e^{Lt} - \nu | L^{-1} (1 - e^{Lt}). \quad (5.6)$$

Here L is the matrix with elements L_{ij} given by (5.4), and L^{-1} is its inverse. If L is singular, $L^{-1}(1 - e^{Lt})$ is to be understood in the sense of a limit.

Passing now to the solution of (5.3), we observe that the method of characteristics is applicable; the characteristics are

$$e^{Lt} | w \rangle = | \phi \rangle, \quad (5.7)$$

where $| \phi \rangle$ is a constant vector. On replacing the w 's by new variables ϕ defined by (5.7), Eq. (5.3) reduces to

$$\partial \Phi / \partial t = \sum_i \nu_i w_i (| \phi \rangle; t) \Phi \equiv \langle \nu | e^{-Lt} | \phi \rangle \Phi. \quad (5.8)$$

Integration of this equation is trivial; reverting to the old variables w , and applying the initial condition

$$\Phi(|w\rangle; 0) = \Phi_0(|w\rangle), \quad (5.9)$$

we finally obtain

$$\Phi(|w\rangle; t) = \exp[-\langle \nu | L^{-1}(1 - e^{Lt}) | w \rangle] \times \Phi_0(e^{Lt}|w\rangle). \quad (5.10)$$

This is the general solution to our problem. Both (5.10) and (5.6) depend on the same matrix operator e^{Lt} . An explicit determination of this operator can be made in the case of harmonic oscillators, with the "dissociation" rate $\mu_i = i\mu$, interacting with a reservoir characterized as in the last section by the constants $\bar{\epsilon}$ and c . This is done in Appendix II. The result is that the double generating function

$$G(u, v; t) = \sum_{i,j} (e^{Lt})_{ij} v^i u^j \quad (5.11)$$

of the matrix elements of e^{Lt} is given by

$$G(u, v; t) = \frac{(\gamma - \alpha)e^{-c't}}{[(\gamma - u) - (\alpha - u)e^{-c't}] - v[\alpha(\gamma - u) - \gamma(\alpha - u)e^{-c't}]}, \quad (5.12)$$

where the constants c' , c'' , α , γ ($0 < \alpha \leq 1 < \gamma$) are defined in Appendix II. The eigenvalues of L appearing in the spectral expansion of e^{Lt} are

$$l_k = -[kc' + c'']; \quad k = 0, 1, \dots \quad (5.13)$$

The corresponding column and row eigenvectors, $|p(k)\rangle$ and $\langle q(k)|$, given in (A II.25) and (A II.26), respectively, form a complete set in terms of which (5.10) can be expressed. Thus

$$\Phi(|w\rangle; t) = \exp\left(-\sum_k \langle \nu | p(k) \rangle \frac{1 - e^{l_k t}}{l_k} \langle q(k) | w \rangle\right) \times \Phi_0\left(\sum_k e^{l_k t} |p(k)\rangle \langle q(k)| w\rangle\right). \quad (5.14)$$

Neither (5.14) nor the expressions for the correlations, etc. that follow from it simplify appreciably when we use the specific eigenvectors and eigenvalues for our problem. Therefore, in the following we shall restrict ourselves to a consideration of the qualitative differences in asymptotic behavior between (5.14) with $\mu \neq 0$, $\nu \neq 0$ and the special case for which $\mu = \nu = 0$ (which was treated in Sec. IV).

When $\mu \neq 0$, all the l_k are negative so that $\exp(l_k t) \rightarrow 0$ as $t \rightarrow \infty$, and

$$\Phi(|w\rangle; \infty) = \exp[-\sum_k \langle \nu | p(k) \rangle l_k^{-1} \langle q(k) | w \rangle]. \quad (5.15)$$

Here we have made use of the fact that

$$[\Phi_0(|w\rangle)]_{w_1=w_2=\dots=0} \equiv [\Phi_0(|z\rangle)]_{z_1=z_2=\dots=1} = 1.$$

Evidently (5.15) can be separated into factors, each of which contains only one w_i . Recalling that $w_i = z_i - 1$, we can rewrite (5.15) as

$$\Phi(|z\rangle; \infty) = \prod_{i=0}^{\infty} \Phi_i(z_i; \infty), \quad (5.16)$$

where

$$\Phi_i(z_i; \infty) = \exp[-\sum_k \langle \nu | p(k) \rangle l_k^{-1} q_i(k) (z_i - 1)]. \quad (5.17)$$

Correspondingly,

$$P(\langle n |; \infty) = \prod_{i=0}^{\infty} P_i(n_i; \infty), \quad (5.18)$$

where

$$P_i(n_i; \infty) = e^{-\bar{n}_i} \bar{n}_i^{n_i} / n_i!, \quad (5.19)$$

and

$$\bar{n}_i \equiv \bar{n}_i(\infty) = -\sum_k \langle \nu | p(k) \rangle l_k^{-1} q_i(k); \quad (5.20)$$

that is, the occupation numbers n_i have *independent* Poisson distributions with means \bar{n}_i given by (5.20).

This may be contrasted with the case $\mu = \nu = 0$, for which (5.14) goes over into the form (3.31) when $t = \infty$.⁴¹ In this case the n_i are correlated since the total number of relaxing particles is fixed, though the correlation tends to zero as the total number of particles becomes very large.

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APPENDIX I

In the infinite dimensional case, the necessary and sufficient conditions for the uniqueness of the solution $T(t)$ to Eqs. (3.11) and (3.12) have been established only for a special class of Λ matrices (occurring in the theory of birth and death processes), and with the requirement that the elements $T_{ij}(t)$ remain non-negative and bounded.⁴² But in most physical problems one may safely assume that the Λ matrix is such as to lead to a unique solution $T(t)$ satisfying these constraints. In our case, the constraints arise from the physical significance of the \bar{n}_i : These are average occupation numbers and hence are non-negative and cannot exceed the total number of particles.

It is not clear that similar reasons exist to constrain the elements of the matrix which appears in the solution (3.20) of (3.19), because the z 's are auxiliary variables with no physical significance. This causes no difficulty, however, because this matrix must be identical with that in (3.10)—as we have already indicated by the

⁴¹ Note that for $\mu = \nu = 0$, we have $l_0 \rightarrow \lambda_0 = 0$; $l_k \rightarrow \lambda_k < 0$ for $k = 1, 2, \dots$; $|p(k)\rangle \rightarrow |x(k)\rangle$; and $\langle q(k)| \rightarrow \langle y(k)|$.

⁴² S. Karlin and J. McGregor, Proc. Natl. Acad. Sci. **41**, 387 (1955); also, W. Feller, Ann. Math. **65**, 527 (1957).

use of the same notation $T(t)$ in both cases—on account of the relation (2.9) between Φ and \bar{n}_i .

The spectral representation (3.14) of $T(t)$ is valid when Λ is finite dimensional and has a complete set of eigenvectors. When Λ is of infinite dimensionality, a spectral representation for $T(t)$ as a sum involving a denumerable set of eigenvalues λ_k cannot always be found; in fact, the representation may be an integral with respect to a continuous variable λ over a finite or infinite region. Examples of simple matrices Λ with both discrete and continuous spectra are given by Ledermann *et al.*⁴³ We shall, however, assume that all Λ matrices of interest to us have discrete spectra.

It may be mentioned here that the particular matrix Λ considered in detail in Sec. IV does satisfy the conditions for uniqueness of $T(t)$, given by Karlin and McGregor.⁴² It also has a discrete spectrum and hence (3.14) is valid. The matrix L , Eq. (A II.2), is of a more general type than the matrices considered in the literature, but it too satisfies all our assumptions.

APPENDIX II

To obtain the spectral decomposition (for the case $\mu_i = i\mu$) of the operator e^{Lt} appearing in (5.10), we shall consider the solution of the matrix equation

$$(d/dt)\langle \bar{n}(t) | = \langle \bar{n}(t) | L, \quad (\text{A II.1})$$

where

$$L = c \begin{pmatrix} -\epsilon_- & \epsilon_- & 0 & \dots \\ \epsilon_+ & -(\epsilon_+ + 2\epsilon_- + \mu/c) & 2\epsilon_- & \dots \\ 0 & 2\epsilon_+ & -(2\epsilon_+ + 3\epsilon_- + 2\mu/c) & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (\text{A II.2})$$

The results required in Sec. IV will then be obtained as a special case by setting $\mu=0$ [in which case L reduces to the matrix of (4.6)].

We observe by comparison with (5.5) that (A II.1) describes the changes that occur in the mean occupation numbers \bar{n}_i of harmonic oscillators in states i through “dissociation” and through collisions with reservoir oscillators. Note that

$$\sum_i \bar{n}_i(t) \leq \sum_i \bar{n}_i(0) = N_0, \quad (\text{A II.3})$$

where N_0 is the finite number of initial particles in the relaxing system. The equality sign in (A II.3) holds when $\mu=0$ (no “dissociation”).

Consider now the formal solution of (A II.1) in the form

$$\langle \bar{n}(t) | = \sum_k \langle \bar{n}(0) | p(k) \rangle e^{l_k t} \langle q(k) |, \quad (\text{A II.4})$$

⁴³ W. Ledermann and G. E. H. Reuter, Phil. Trans. Roy. Soc. (London) A246, 321 (1953–54).

⁴⁴ It is clear from inspection of (A II.2) that any number whatever is an eigenvalue of L since, for any l , one can construct the components of the associated eigenvector by solving the resultant system of linear equations recursively. However, since the elements of allowable eigenfunctions are restricted by (A II.3), we obtain the discrete spectrum (A II.22).

where the l_k are eigenvalues of L , and $|p(k)\rangle$ and $\langle q(k)|$ are the corresponding column and row eigenvectors. We want to determine these. This is most easily done in terms of generating functions. Define the generating function

$$G(u; t) = \sum_{i=0}^{\infty} \bar{n}_i(t) u^i \equiv \langle \bar{n}(t) | u \rangle, \quad (\text{A II.5})$$

where $|u\rangle$ is a column vector with elements $u_i = u^i$. In view of (A II.3), the generating function G is certainly analytic for $u \leq 1$. From (A II.4) we then have

$$G(u; t) = \sum_k \langle \bar{n}(0) | p(k) \rangle e^{l_k t} G_R(u, k), \quad (\text{A II.6})$$

where

$$G_R(u, k) = \langle q(k) | u \rangle \quad (\text{A II.7})$$

is the generating function of the elements of the row eigenvector $\langle q(k) |$ of L . If we denote by $G(u, v; t)$ the special case of (A II.6) corresponding to the particular initial conditions

$$\bar{n}_i(0) = v^i; \quad v < 1, \quad (\text{A II.8})$$

then

$$G(u, v; t) = \sum_k G_C(v, k) e^{l_k t} G_R(u, k), \quad (\text{A II.9})$$

where

$$G_C(v, k) \equiv \langle v | p(k) \rangle \equiv \sum_i v^i p_i(k) \quad (\text{A II.10})$$

is the generating function of the elements of the column eigenvector $|p(k)\rangle$.

To obtain the eigenvalues l_k , and the corresponding eigenfunctions $|p(k)\rangle$ and $\langle q(k)|$ (via their respective generating functions G_C and G_R), we need only use the method of generating functions to solve (A II.1) with the special initial conditions (A II.8), and then expand the function $G(u, v; t)$ thus obtained, in the form (A II.9). We proceed to do this below.

It can easily be shown from (A II.1) and (A II.2) that the equation satisfied by $G(u; t)$ is

$$\partial G / \partial t = c\epsilon_- (u - 1) + [c\epsilon_- u^2 - (2c\bar{\epsilon} + \mu)u + c\epsilon_+] \partial G / \partial u. \quad (\text{A II.11})$$

The characteristic equation for this first order partial differential equation is

$$dt = - \frac{du}{c\epsilon_- u^2 - (2c\bar{\epsilon} + \mu)u + c\epsilon_+} = - \frac{du}{c\epsilon_- (u - \alpha)(u - \gamma)}, \quad (\text{A II.12})$$

where

$$\alpha = \frac{1}{2c\epsilon_-} [2c\bar{\epsilon} + \mu - (c^2 + \mu^2 + 4c\bar{\epsilon}\mu)^{\frac{1}{2}}] \quad (\text{A II.13})$$

$$\beta = \frac{1}{2c\epsilon_-} [2c\bar{\epsilon} + \mu + (c^2 + \mu^2 + 4c\bar{\epsilon}\mu)^{\frac{1}{2}}].$$

The solution of (A II.12) is

$$\left(\frac{u-\alpha}{u-\gamma}\right)e^{-c\epsilon_-(\gamma-\alpha)t}=\psi=\text{constant.} \quad (\text{A II.14})$$

On using ψ as a new variable instead of u , Eq. (A II.11) reduces to

$$\left(\frac{\partial G}{\partial t}\right)_\psi = c\epsilon_- \left(\frac{\gamma\psi - \alpha e^{-c't}}{\psi - e^{-c't}} - 1\right)G, \quad (\text{A II.15})$$

where $c' = c\epsilon_-(\gamma-\alpha)$. The solution to this equation is

$$G = e^{c\epsilon_-(\gamma-1)t}(\psi - e^{-c't})h(\psi), \quad (\text{A II.16})$$

where $h(\psi)$ is an arbitrary function of ψ , to be determined by the initial condition. If the latter is

$$G(u; 0) = \sum_i \bar{n}_i(0)u^i = G_0(u), \quad (\text{A II.17})$$

we finally obtain

$$G(u; t) = \frac{(\gamma-\alpha)e^{-c't}}{(\gamma-u)-(\alpha-u)e^{-c't}} \times G_0\left(\frac{\alpha(\gamma-u)-\gamma(\alpha-u)e^{-c't}}{(\gamma-u)-(\alpha-u)e^{-c't}}\right), \quad (\text{A II.18})$$

where $c'' = c\epsilon_-(1-\alpha)$.

This gives the generating function of the $\bar{n}_i(t)$ for arbitrary initial conditions. To determine the eigenvalues and eigenvectors we now consider the special condition (A II.8) for which

$$G_0(u) = 1/(1-uv). \quad (\text{A II.19})$$

Hence,

$$G(u, v; t) = \frac{(\gamma-\alpha)e^{-c't}}{[(\gamma-u)-(\alpha-u)e^{-c't}] - v[\alpha(\gamma-u)-\gamma(\alpha-u)e^{-c't}]}, \quad (\text{A II.20})$$

$$= \sum_{k=0}^{\infty} (\gamma-\alpha) \frac{(\alpha-u)^k}{(\gamma-u)^{k+1}} \frac{(1-v\gamma)^k}{(1-v\alpha)^{k+1}} \times \exp\{-[kc' + c'']t\}. \quad (\text{A II.21})$$

Comparing this with (A II.9), we deduce that

$$l_k = -[kc' + c''], \quad k=0, 1, \dots, \quad (\text{A II.22})$$

$$G_C(v, k) = (1-v\gamma)^k (1-v\alpha)^{-k-1}, \quad (\text{A II.23})$$

and

$$G_R(u, k) = (\gamma-\alpha)(\alpha-u)^k(\gamma-u)^{-k-1}. \quad (\text{A II.24})$$

Using the identity (4.11), we expand the last two equations in powers of v and u , respectively, and obtain

$$p_i^k = \gamma^i {}_2F_1(-i, k+1; 1; 1-\alpha/\gamma), \quad (\text{A II.25})$$

and

$$q_j^k = (1-\alpha/\gamma)(\alpha/\gamma)^k \times \alpha^{-j} {}_2F_1(-j, k+1; 1; 1-\alpha/\gamma). \quad (\text{A II.26})$$

Since

$$G(u, v; t) = \langle v | e^{L_t} | u \rangle, \quad (\text{A II.27})$$

a direct expansion of (A II.20) in powers of u and v [rather than in powers of the exponential as in (A II.21)] yields the following two alternative expressions for $(e^{L_t})_{ij}$:

$$(e^{L_t})_{ij} = (\gamma-\alpha)e^{-c't} [\alpha\gamma(1-e^{-c't})]^{i-j}, \quad (\text{A II.28a})$$

or

$$(e^{L_t})_{ij} = (\gamma-\alpha)e^{-c't} (1-e^{-c't})^{i-j} (\alpha-\gamma e^{-c't})^j \times (\gamma-\alpha e^{-c't})^{-j-1} {}_2F_1(-i, j+1; 1; s), \quad (\text{A II.28b})$$

where

$$s = \frac{(\gamma-\alpha)^2 e^{-c't}}{(\gamma-\alpha e^{-c't})(\gamma e^{-c't}-\alpha)}. \quad (\text{A II.29})$$

To obtain the results used in Sec. IV, we set $\mu = \nu = 0$ in the above formulas, so that

$$\alpha = 1, \quad \gamma = \epsilon_+/\epsilon_-, \quad (\text{A II.30})$$

$$c' = c, \quad c'' = 0,$$

and the expressions (A II.22), (A II.23), and (A II.24) for l_k , G_C , and G_R go over into (4.12), (4.14), and (4.13), respectively. The expressions (4.9a, b) for $T_{ij} \equiv (e^A)_{ij}$ are obtained from (A II.28a, b).