cannot expect better results than 4.27 ev so long as we do not take account of angular correlation.

According to our method, we obtain a dissociation energy of $4.4\sim4.6$ ev considering only two structures. In these calculations, the angular correlation is considered in the ionic term Ξ_i because Ξ_i is made up from the exact eigenfunction of the H^- ion. The angular correlation, of course, becomes large when electrons approach each other and this chance is high in the ionic structure. If the ionic structure is made up from the exact one in order to take account of the angular correlation in the ionic structure, therefore, most of the angular correlation energy of 0.45 ev will be included in the results. This is the reason why we obtain refined results which are better than 4.27 ev and the coefficient c of the ionic term is larger than that of the orbital treatments.

In the orbital approaches of the H^- ion or He atom, the treatment of the configuration interaction far from success to take account of the correlation energy[9] and this situation may be also true in the molecular problems. Nevertheless in our method such a difficulty is overcome because the ionic term is made up from the exact function. This fact is an advantage of the present method. We should, here, only take care of the ionic structure to be the well-matched function in order to make the configuration interaction effective.

In this paper, the hydrogen-like functions have been used as the best approximate functions for the convenience of the calculation. Weinbaum[10] has obtained a dissociation energy of 4.02 ev using these functions in the orbital treatment. This result seems to be not so bad when compared with James and Coolidge's result of 4.27 ev because both have larger error in the angular correlation. Therefore, it seems, that the molecular wave function made up from those of the constituent atoms or ions are rather favorable even if only a few structures are considered, and in our problems, the hydrogen-like functions are not bad for the basic functions of the best approximate functions.

Of course, improved orbital functions for the best approximate functions and the higher structures may be necessary for improving our results. It may be also useful to determine the best effective charges Z_n and Z_i within the limit of the present treatment. However our method is accompanied with inevitable error numerically because of the treatment of the interaction operator. Then these higher order refinements may be sometimes covered by the error and will be meaningless.

5. ACKNOWLEDGMENTS

The author expresses his sincere thanks to Professor M. Kotani for his continuous encouragement and deep interest in this work and to Mr. K. Ohno and Mr. T. Itoh for presenting their unpublished work.

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[9] G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U. S. 38, 154 (1952); Green, Mulder, Ufford, Slaymaker, Krawitz, and Mertz, Phys. Rev. 85, 65 (1952).

[10] S. Weinbaum, J. Chem. Phys. 1, 593 (1933).

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Studies in Nonequilibrium Rate Processes.* I. The Relaxation of a System of Harmonic Oscillators

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As a part of an investigation of nonequilibrium phenomena in chemical kinetics a theoretical study has been made of the collisional and radiative relaxation of a system of harmonic oscillators contained in a constant temperature heat bath and prepared initially in a vibrational nonequilibrium distribution. An exact solution has been obtained for the general relaxation equation applicable to this system and expressions have been derived for the relaxation of initial Boltzmann distributions, Poisson distributions, and δ-function distributions as well as for the relaxation of the moments of the distributions. Using the latter result, explicit expressions are given for the relaxation of the internal energy of the system of oscillators and for the time dependence of the dispersion of the distributions.

1. INTRODUCTION

IT has been recognized for many years that by its very nature a chemical reaction must produce a perturbation in the initial Maxwell-Boltzmann distribution of the reactant species.[1] The extent of the departure from equilibrium will depend upon the relative magnitudes of the rates of the elementary chemical reactions (i.e., the rate of transformation of reactants

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[1] See, e.g., R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1949), Chap. XII, or Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), Chap. XVI.

to products) and the rates of energy exchange between the various atomic and molecular species in the reaction system. If the rate of the chemical transformation is small compared with the rate of energy exchange, the perturbation of the initial equilibrium distribution will be small and the reaction system can be discussed in terms of equilibrium statistical mechanics. If, however, the rate of the chemical transformation exceeds the rate of intra- and intermolecular energy exchange, there may develop a considerable perturbation of the equilibrium Maxwell-Boltzmann distribution of energy during the course of the chemical reaction. Under these conditions the equilibrium hypothesis underlying the present collision and absolute rate theories of chemical kinetics may no longer be tenable. Recent experimental work on various rapid high-temperature chemical reactions has shown quite clearly that there is indeed in many cases a considerable perturbation of the initial equilibrium distribution of energy during the course of the chemical reaction.[2] It therefore becomes important to study the distribution of energy in a reaction system during the course of a chemical reaction so that a foundation can be laid for the development of a nonequilibrium theory of chemical kinetics.

The specific problem which we wish to consider in the above context concerns the relaxation of the distribution of a system of harmonic oscillators prepared initially in nonequilibrium vibrational distributions. The oscillators are excited to these distributions either by external perturbations, such as irradiation with short duration, high intensity light or by the passage of a shock wave, or internally by some specific chemical reaction.[3] After the external perturbation has been removed (i.e., after the light has been turned off or after the passage of the shock wave) or after the cessation of the reaction, the system of oscillators will relax to its final equilibrium distribution by inelastic collisions and by radiative transitions. We wish to study in detail the dynamic behavior of the distribution and of the moments of the distribution of the oscillators among their energy levels for various initial nonequilibrium distributions.

Our study of the relaxation of a system of harmonic oscillators is based on the following model:

(a) The oscillators are contained in a large excess of (chemically) inert gas which acts as a *constant temperature* heat bath throughout the relaxation process. This implies that the concentration of the excited oscillators is sufficiently small and the energy absorbed by them during their excitation is sufficiently small that the heat bath remains at its initial equilibrium temperature T throughout the relaxation process.

(b) The total concentration of excited oscillators is sufficiently small so that the relaxation process is first order with respect to the concentration of oscillators. The energy exchange which controls the relaxation thus takes place primarily between the oscillators and the heat bath.

(c) The excited oscillators can transfer their vibrational energy both by collision and by radiation. In the collisional transfer of energy, the vibrational energy of the excited oscillators can be exchanged with both the translational and the vibrational degrees of freedom of the heat bath molecules.

(d) The collisional transition probabilities for transitions between the vibrational levels i and j of the harmonic oscillators are to be calculated according to the prescription of Landau and Teller.[4] According to this prescription, the perturbations which induce the transitions are linear in the normal coordinate (i.e., the internuclear separation in the case of a harmonic oscillator) and sufficiently small for a first order perturbation calculation. With these assumptions, the matrix elements for collisional transitions are identical, except for a constant factor, with those for the radiative transitions of a harmonic oscillator. The same "selection rules" will thus hold for collisional transitions as for radiative ones in that the collision induced transitions of the oscillators will take place only between adjacent vibrational levels. The collisional transition probabilities per collision, $P_{i,j}$ are thus given by

$$\begin{aligned} &P_{i,j}=P_{j,i}, \quad P_{i,j}=0 \quad \text{for} \quad j\neq\begin{cases} i+1 \\ i-1 \end{cases} \\ &P_{i,j+1}=(i+1)P_{10}, \end{aligned} \tag{1.1}$$

where P_{10} is the collisional transition probability per collision for transitions between vibrational levels $i=1$ and $i=0$.

We now wish to derive the differential equations which govern the relaxation of the ensemble of harmonic oscillators in our model. It has been pointed out by Herzfeld[5] that an exact energy balance in a relaxation process of the type discussed here can be obtained when either (a) the excited system or the heat bath have a nearly continuous array of levels or (b) the excited system and the heat bath have equidistant energy levels and exchange only vibrational energy. Under either of these conditions, a transition $-\Delta E$ between two states in the excited system can be matched by a transition of a corresponding energy ΔE between two states of the heat bath. This latter case can readily be realized if one chooses for the relaxation system an

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[2] For a more detailed discussion of this point see K. E. Shuler, J. Phys. Chem. **57**, 396 (1953); *5th Symposium (International) on Combustion* (Reinhold Publishing Corporation, New York, 1955), pp. 56–74.

[3] An example of the latter process is the formation of OH in the vibrational state $v=9$ in the reaction $H+O_3 \rightarrow OH+O_2$ studied by A. B. Meinel, J. Astrophys. **111**, 207, 433, 555 (1950) and by McKinley, Garvin, and Boudart, J. Chem. Phys. **23**, 784 (1955).

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

[5] K. F. Herzfeld in *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1955), p. 233.

ensemble of harmonic oscillators of which a small fraction are excited to an initial vibrational nonequilibrium distribution while the large excess of unexcited oscillators serves as the heat bath. If we let

$x_n(t)$ = fraction of excited oscillators in level n
y_i = concentration of heat bath oscillators in level i

$P_{n,\,n+1;\,i,\,i-1}$ = probability per collision for the energy transfer $n \to n+1$ as $i \to i-1$

the relation equation can be written as

$$\frac{dx_n(t)}{dt}=-Z\Big[x_n\Big(\sum_{i=0}^{\infty} y_iP_{n,\,n+1;\,i,\,i-1}+\sum_{i=0}^{\infty} y_iP_{n,\,n-1;\,i,\,i+1}\Big)-x_{n+1}\sum_{i=0}^{\infty} y_iP_{n+1,\,n;\,i,\,i+1}-x_{n-1}\sum_{i=0}^{\infty} y_iP_{n-1,\,n;\,i,\,i-1}\Big] \quad (1.2)$$

where Z is the collision number, i.e., the number of collisions per second suffered by the oscillator in the level system $n=0, 1, \cdots$ when the gas density is one molecule per unit volume. Using Eq. (1.1), the probabilities $P_{n,\,n+1;\,i,\,i-1}$ for concurrent collisional transitions can be written as

$$\begin{aligned} P_{n,\,n+1;\,i,\,i-1}&=(n+1)iP_{10}\\ P_{n,\,n-1;\,i,\,i+1}&=n(i+1)P_{10} \end{aligned} \quad (1.3)$$

so that Eq. (1.2) becomes

$$\frac{dx_n(t)}{dt}=-ZP_{10}\Big[(n+1)x_n\sum_{i=0}^{\infty} iy_i+nx_n\sum_{i=0}^{\infty}(i+1)y_i-(n+1)x_{n+1}\sum_{i=0}^{\infty}(i+1)y_i-nx_{n-1}\sum_{i=0}^{\infty} iy_i\Big] \quad (1.4)$$
$$n=0, 1, 2, \cdots.$$

Since we assume that the heat bath remains in its initial Boltzmann distribution at temperature T throughout the relaxation process we can write, for all times t,

$$y_i=N(1-e^{-\theta})e^{-i\theta} \quad (1.5)$$

where N is the total concentration of oscillators in the heat bath and where $\theta=h\nu/kT$ and ν is the fundamental frequency of the oscillators. Substitution of (1.5) into (1.4) finally leads to

$$dx_n(t)/dt=k_{10}(1-e^{-\theta})^{-1}\{ne^{-\theta}x_{n-1}-[n+(n+1)e^{-\theta}]x_n+(n+1)x_{n+1}\} \quad n=0, 1, 2, \cdots \quad (1.6)$$

where $k_{10}=ZP_{10}N$ is the collisional transition probability per second for transitions between levels 1 and 0 of the oscillators. The set of differential difference equations (1.6) governs the relaxation of a system of excited harmonic oscillators contained in a harmonic oscillator heat bath (with $\nu_n=\nu_i$) when there is only vibrational energy exchange between the excited oscillators and the heat bath.

It is not possible to follow the method used above to obtain Eq. (1.6) when the relaxation proceeds by the interchange of the vibrational energy of the excited oscillators with the translational energy of the heat bath. In this case it is not possible to establish internal equilibrium by considering only the energy transfer between the excited oscillators and the heat bath as was done previously since the oscillators will give up their excitation energy only in quanta of $h\nu$ while the heat bath has a nearly continuous array of translational energy states. Furthermore, it is not possible to write down simple explicit expressions for the joint transition probabilities $P_{n;\,i}$ as was done in (1.3), where i now refers to the translational energy levels of the heat bath, within the framework of the Landau-Teller approximation used in our model. It has been shown, however, by Rubin and Shuler[6] that the set of differential difference equations governing the relaxation process now under discussion can be obtained by the method used by Fowler in discussing the equilibrium relationship between collisions of the first and second kind.[7] Using properties (a) to (d) of our model and applying the principle of detailed balancing at equilibrium, Rubin and Shuler showed that the relaxation equation for the case when the relaxation proceeds by the interchange of the vibrational energy of the excited oscillators with the translational energy of the heat bath has the form of (1.6) except for the absence of the factor $(1-e^{-\theta})^{-1}$ in front of the braces (see Appendix II).

A third relaxation mechanism involves the interchange of radiation between the excited oscillators and the heat bath. The relaxation equations for this case have been derived by Rubin and Shuler[8] by considering the interaction of the oscillators with a radiation heat bath in equilibrium with the heat bath at the temperature T. Using the Einstein coefficients A and B for spontaneous and induced emission and for absorption and Planck's radiation law for the density of the radiation, it could readily be shown that the relaxation equation for radiative transitions is again of the form of (1.6) but with k_{10} replaced by A_{10}, the Einstein coefficient for spontaneous emission between vibrational levels 1 and 0 of the oscillators.[9]

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[6] R. J. Rubin and K. E. Shuler, J. Chem. Phys. 25, 59 (1956).

[7] R. H. Fowler, Phil. Mag. 47, 257 (1924).

[8] R. J. Rubin and K. E. Shuler, J. Chem. Phys. 26, 137 (1957).

[9] It should be noted that the case of radiative relaxation could also be discussed in terms of the transfer of photons with energy $h\nu$ between the excited oscillators and the heat bath oscillators by the method used above for the transfer of vibrational energy and without recourse to the radiation field. The exact correspondence between these two relaxation process explains the exact correspondence between the equations describing the two processes when the appropriate transition probabilities, i.e., k_{10} or A_{10}, are used in Eq. (1.1). It should also be noted that an internal energy balance can be maintained for this relaxation process.

The general relaxation equation applicable to the relaxation of a system of harmonic oscillators in a constant temperature heat bath can finally be written as

$$\frac{dx_n(t)}{dt}=\kappa\{ne^{-\theta}x_{n-1}-[n+(n+1)e^{-\theta}]x_n+(n+1)x_{n+1}\}\qquad n=0,1,2,\cdots \quad (1.7)$$

where

$$k=\begin{cases}k_{10}(1-e^{-\theta})^{-1} & \text{for collisional vibration-vibration exchange}\\ k_{10}' & \text{for collisional vibration-translation energy exchange}\\ A_{10}(1-e^{-\theta})^{-1} & \text{for radiative energy exchange.}\end{cases}\quad (1.7\text{a})$$

It is the object of this paper to obtain an exact solution of (1.7) subject to the condition $\sum x_n(t)=1$ (closed system) for various initial distributions $x_n(0)$.

Rubin and Shuler[6] obtained a solution of (1.7) for the special case $\theta\ll 1$, which, in essence, corresponds to replacing the discrete set of energy levels by a quasi-continuum, by approximating the set of differential difference equations (1.7) by the related partial differential equation which then admitted of a solution in terms of a Fourier development in Laguerre polynomials. The choice of $\theta\ll 1$, made by Rubin and Shuler for mathematical convenience, is realized physically only for very few molecules and then only at rather high temperatures. Thus, for instance, one finds $\theta=h\nu/kT=60/T$ for Cs_2 so that the inequality $\theta\ll 1$ can be fulfilled for $T>10^3$ °K. For most diatomic species, however, $\theta>1$ at ordinary temperatures (300–1000°K). Some examples are NO$(\theta=2.73\cdot 10^3/T)$, CO$(\theta=2.13\cdot 10^3/T)$, and OH$(\theta=5.37\cdot 10^3/T)$, where the frequencies ν correspond to the electronic ground states. For a heat bath at 300°K, one thus finds $\theta\sim 10$ to 20. We will show in the appendix that the general solution of (1.7), valid for all θ, reduces to the solution of Rubin and Shuler when $\theta\rightarrow 0$. The qualitative characteristics of relaxation from various initial distributions as determined by the small θ theory are in general agreement with the exact results derived below.

We shall show in Sec. 2 that the exact solution of (1.7) can be written in terms of the generating function

$$G(z,t)=\sum_{n=0}^{\infty}z^n x_n(t) \quad (1.8)$$

and the dimensionless time $\tau=\kappa t(1-e^{-\theta})$ as

$$G(z,t)=\frac{(e^{\theta}-1)}{(z-1)e^{-\tau}-(z-e^{\theta})}\times G_0\left[\frac{(z-1)e^{-\tau}e^{\theta}-(z-e^{\theta})}{(z-1)e^{-\tau}-(z-e^{\theta})}\right] \quad (1.9)$$

where $G_0(y)\equiv G(y,0)$ is determined by the initial condition (distribution) $x_n(0)$ and where $x_n(t)$, the fraction of the molecules in level n is the coefficient of z^n in (1.9). We consider in this study the relaxation of three initial nonequilibrium distributions which could readily be obtained in a physical system and the relaxation of their moments:

(1) An initial Boltzmann distribution with temperature $T_0\neq T$ for which $x_n(0)$ is given by

$$x_n(0)=[1-\exp(-\theta_0)]\exp(-n\theta_0) \quad (1.10)$$

where $\theta_0=h\nu/kT_0$. Substitution of (1.10) into (1.9) yields the Boltzmann distribution (for details see Sec. 4)

$$x_n(t)=[1-\exp(-\Theta)]\exp(-n\Theta) \quad (1.11)$$

with

$$\Theta=\log\left[\frac{e^{-\tau}(1-e^{\theta-\theta_0})-e^{\theta}(1-e^{-\theta_0})}{e^{-\tau}(1-e^{\theta-\theta_0})-(1-e^{-\theta_0})}\right]. \quad (1.12)$$

At early times

$$\Theta\sim\theta+\tau\frac{(1-e^{\theta-\theta_0})}{(1-e^{\theta})}(e^{\theta_0}-1)+O(\tau^2) \quad (1.12\text{a})$$

and as $\tau\rightarrow\infty$

$$\Theta\sim\theta+e^{-\tau}\left[\frac{(1-e^{-\theta})}{(1-e^{-\theta_0})}(1-e^{\theta-\theta_0})\right]+O(e^{-2\tau}).$$

The initial Boltzmann distribution (1.10) thus relaxes to a final equilibrium Boltzmann distribution via the continuous sequence of Boltzmann distributions (1.11). Since the transient distribution of the relaxing oscillators is always canonical in this case, it is possible to characterize it by a "temperature" $\mathcal{T}(t)=h\nu/k\Theta(t)$. To give an indication of the relaxation of this "temperature" we have plotted Θ^{-1} as a function of time for various initial and final temperatures T_0 and T in Fig. 1.[10]

An interesting feature of the curves in Fig. 1 is that the relaxation time associated with the temperature rise from $T_1\rightarrow T_2(\theta_2<\theta_1)$ is less than that for the corresponding temperature drop $T_2\rightarrow T_1$ (see curves A and B). Qualitatively this is not surprising because more levels are available for occupation at the higher temperature equilibrium than at the lower. The system becomes "disordered" faster than it can be ordered.

(2) An initial Poisson distribution with

$$x_n(0)=e^{-a}a^n/n! \quad (1.13)$$

where a is the mean value $\bar{n}$ of the level number n. This represents a "peaked" initial distribution, $x_n(0)$, in which most of the excited oscillators are found initially in levels near $n=a$. The level population $x_n(t)$ resulting

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[10] The persistence of the form of the Boltzmann distribution is a consequence of the Landau-Teller transition probabilities. It has been shown by Rubin and Shuler, J. Chem. Phys. 24, 68 (1956), that other choices of transition probabilities will lead to a different relaxation behavior.

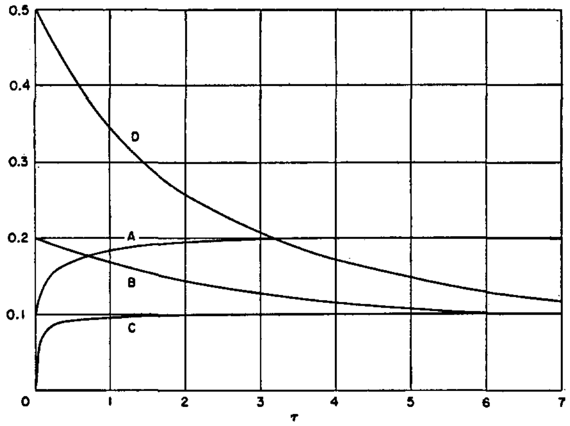

FIG. 1. The "temperature" $\mathcal{T}k/h\nu=\Theta^{-1}$ as a function of time τ for the relaxation of initial Boltzmann distributions [Eq. (1.12)]

Curve A: $\theta_0=10$, $\theta=5$, $T_0=\frac{1}{2}T$
Curve B: $\theta_0=5$, $\theta=10$, $T_0=2T$
Curve C: $\theta_0=20$, $\theta=10$, $T_0=\frac{1}{2}T$
Curve D: $\theta_0=2$, $\theta=10$, $T_0=5T$.

from an initial Poisson distribution is found to depend on the nth Laguerre polynomial [Eq. (5.6)]. We have plotted x_n as a function of τ for $\theta=3$ and $a=15$ in Fig. 2. Notice that the distribution narrows with time and shifts toward the equilibrium distribution as $t\to\infty$. We have also plotted $\log x_n$ *vs* t for the Poisson distribution (see Fig. 3) in order to gain some further information about the approach to equilibrium.

(3) An initial δ function distribution with all excited oscillators in state m:

$$\begin{aligned} x_n(0)&=1 \quad \text{when} \quad n=m \\ x_n(0)&=0 \quad \text{when} \quad n\neq m. \end{aligned} \qquad (1.14)$$

The level population $x_n(t)$ is given in terms of hypergeometric functions [see Eq. (6.5)]. The initially sharp distribution broadens and shifts to lower energy states if $m>\bar{n}$ (in a manner similar to that plotted in reference 6 for the case $\theta\ll 1$).

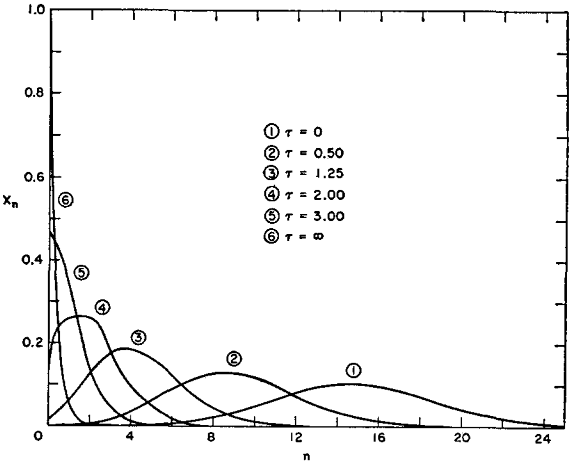

FIG. 2. The relaxation of an initial Poisson distribution $x_n(0)=e^{-a}a^n/n!$ with $a=\langle n\rangle=15$ to a final Boltzmann distribution with $\theta=3$. The ordinate x_n gives the fraction of oscillators in energy level n.

(4) We have also obtained (see Sec. 3) a solution for the relaxation of the moments of the distribution. The transient behavior of the factorial moments of $x_n(t)$ [Eq. (3.1a)] defined by

$$f_m(t)=\sum_{n=0}^{\infty} n(n-1)\cdots(n-m+1)x_n(t) \qquad m=1,2,\cdots \qquad (1.15)$$

is described by (3.7):

$$\frac{df_m}{\kappa dt}+m(1-e^{-\theta})f_m=m^2e^{-\theta}f_{m-1}. \qquad (1.16)$$

The internal energy $E(t)$ of our system of excited oscillators is related to the first moment f_1 by

$$E(t)=h\nu\sum_{n=0}^{\infty} nx_n(t)=h\nu f_1. \qquad (1.17)$$

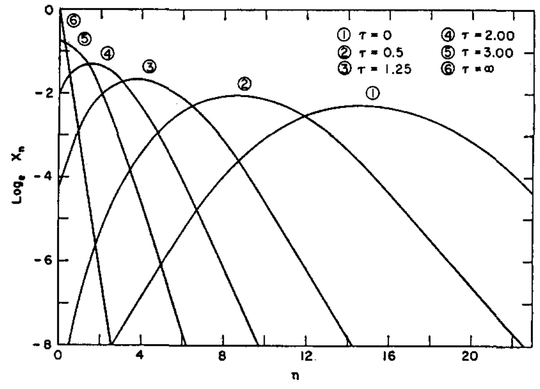

FIG. 3. A plot of $\log x_n$ *vs* n for the relaxation of the initial Poisson distribution shown in Fig. 2. The straight line portions of these curves for high n give a good indication of the adjustment of the initial Poisson distribution (at $\tau=0$) to the equilibrium Boltzmann distribution at $\tau=\infty$.

The combination of Eqs. (1.16) and (1.17) readily leads to the remarkably simple expression of Bethe and Teller[11]

$$\frac{E(t)-E(\infty)}{E(0)-E(\infty)}=e^{-\tau} \qquad (1.18)$$

for the relaxation of the internal energy where $E(\infty)$ is the internal energy which corresponds to the final Boltzmann distribution. It should be noted that according to (1.18), the magnitude of the internal energy at any time t depends only on $E(0)$ and not on the form of the initial distribution $x_n(0)$. The relaxation of the mean energy of a system of harmonic oscillators is therefore determined solely by the amount of energy added to the system and not by its distribution. Hence

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[11] H. A. Bethe and E. Teller, "Deviations from thermal equilibrium in shock waves," Ballistic Research Laboratory, Report X-117, 1941. See also Rubin and Shuler, reference 6.

any description of nonequilibrium distributions (at least for the case of harmonic oscillators) which is based solely on the magnitude of the internal energy $E(t)$ can never give any information (other than $\bar{n}$) about the distribution $x_n(t)$ associated with this energy. From Eq. (1.18) and the definition of τ in (1.8) one obtains

$$t_{\text{relax}}=[\kappa(1-e^{-\theta})]^{-1} \tag{1.19}$$

for the relaxation time of the internal energy.

It is also possible to obtain the time dependence of the dispersion $\sigma^2(t)$, from Eq. (1.16) where

$$\sigma^2(t)=\langle(n-f_1)^2\rangle_{\text{Av}}=f_2+f_1(1-f_1). \tag{1.20}$$

A knowledge of the dependence of the dispersion of the distribution with time is of particular interest in connection with "peaked" initial distributions such as the δ function, Poisson, or Gaussian distributions since it gives some information about the "spreading" or "contraction" of the distribution as it tends toward the equilibrium Boltzmann distribution.

The "easy" problems of nonequilibrium statistical mechanics are those associated with physical systems which can be divided into two parts, (a) the large heat bath with many degrees of freedom which remains at equilibrium (and has the fluctuations expected in a system at equilibrium) and (b) the small nonequilibrium part with relatively few degrees of freedom which relaxes through interactions with the heat bath without disturbing the heat bath equilibrium.

The Einstein theory of Brownian motion is the classical example of this type of situation. The large Brownian particle with an initial δ-function distribution interacts with the surrounding fluid which remains at equilibrium. The theory developed in the present paper follows in the same spirit.[12] Mathematically the relevant equations associated with these processes are linear and can be discussed in considerable detail.

Those processes which do not permit the postulation of an equilibrium heat bath usually lead to nonlinear equations (for example the Boltzmann equation for the transport theory of gases) and have not been discussed in any really satisfactory manner. If the x_n's and y_i's in our Eq. (1.2) were both in a nonequilibrium state (for example by setting $x_i=y_i$) our differential equations would become nonlinear and little could be done with them.

2. GENERAL SOLUTION OF FUNDAMENTAL EQUATION

We solve (1.7) through the introduction of the generating function

$$G(z,t)=\sum_{n=0}^{\infty} z^n x_n(t) \tag{2.1a}$$

which is defined so that the coefficient of z^n is the fraction of molecules in the nth state at time t. We note that

$$\frac{\partial G}{\partial z}=z^{-1}\sum_{n=0}^{\infty} n z^n x_n(t). \tag{2.1b}$$

If we multiply (1.7) by z^n and sum from $n=0$ to $n=\infty$ we find that G satisfies the first-order partial differential equation

$$\frac{1}{\kappa}\frac{\partial G}{\partial t}=(z-1)e^{-\theta}\left\{\frac{\partial G}{\partial z}[(z-1)+(1-e^{\theta})]+G\right\}. \tag{2.2}$$

This equation can be transformed into a somewhat simpler one by letting

$$y=z-1,\quad \lambda=\kappa t e^{-\theta},\quad c=1-e^{\theta}, \tag{2.3a}$$

and

$$H(y,\lambda)=(y+c)G. \tag{2.3b}$$

Then H satisfies

$$g\left(\frac{\partial H}{\partial \lambda},\frac{\partial H}{\partial y}\right)=\frac{\partial H}{\partial \lambda}-y(y+c)\frac{\partial H}{\partial y}=0 \tag{2.4}$$

or, if we let $p_1=\partial H/\partial\lambda$ and $p_2=\partial H/\partial y$

$$g(p_1,p_2)=p_1-y(y+c)p_2=0. \tag{2.5}$$

Following the method of characteristics we consider[13]

$$\frac{dy}{\partial g/\partial p_2}=\frac{d\lambda}{\partial g/\partial p_1} \tag{2.6a}$$

or

$$d\lambda=-dy/y(y+c) \tag{2.6b}$$

whose solution

$$ye^{\lambda c}[y+c]^{-1}=\text{constant} \tag{2.6c}$$

implies that the general solution of (2.4) is

$$H(y,\lambda)=f(y[y+c]^{-1}e^{\lambda c}) \tag{2.7}$$

where f is an arbitrary function which is to be determined from the initial distribution $\{x_n(0)\}$.

The general solution of (2.2) is then

$$\begin{aligned}G(z,t)=&(z-e^{\theta})^{-1}\\ &\times f\{[z-1][z-e^{\theta}]^{-1}\exp[-t\kappa(1-e^{-\theta})]\}.\end{aligned} \tag{2.8}$$

It is to be noted that the definition of (2.1a) implies $G(1,t)=\sum x_n(t)=1$. Hence

$$f(0)=(1-e^{\theta}). \tag{2.9}$$

The initial distribution $x_n(0)$ characterizes $G(z,0)$. The function f is related to $G_0(z)\equiv G(z,0)$ by setting

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[12] The general theory of the "easy" problems has been discussed recently by many authors: M. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945); H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951); P. Bergmann and J. Lebowitz, Phys. Rev. **99**, 578 (1955); and others. A brief review and bibliography of this subject has been prepared by E. Montroll and M. S. Green, Ann. Rev. Phys. Chem. **5**, 449 (1954).

[13] F. S. Woods, *Advanced Calculus* (Ginn and Company, New York, 1934), p. 292.

$t=0$ in (2.8) so that

$$f([z-1][z-e^{\theta}]^{-1})=(z-e^{\theta})G_0(z) \tag{2.10}$$

or

$$f(\eta)=\left(\frac{e^{\theta}-1}{\eta-1}\right)G_0\left(\frac{\eta e^{\theta}-1}{\eta-1}\right). \tag{2.11}$$

Clearly, if we let

$$\tau=\kappa t(1-e^{-\theta}) \tag{2.12}$$

we can express $G(z,t)$ as

$$G(z,t)=\frac{1-e^{\theta}}{(z-e^{\theta})-(z-1)e^{-\tau}} \times G_0\left(\frac{(z-1)e^{-\tau}e^{\theta}-(z-e^{\theta})}{(z-1)e^{-\tau}-(z-e^{\theta})}\right). \tag{2.13}$$

In principle our problem is solved because G_0 is determined by the initial conditions and our $x_n(t)$'s are coefficients of z^n in (2.13). As $t\rightarrow\infty$ (and hence as $\tau\rightarrow\infty$) we have, since $G(1,t)=1=G_0(1)$ for all t,

$$G(z,\infty)=(1-e^{-\theta})/(1-ze^{-\theta}). \tag{2.14a}$$

Hence by (2.1a) the equilibrium distribution is

$$x_n(\infty)=(1-e^{-\theta})e^{-n\theta} \tag{2.14b}$$

which is the Boltzmann distribution of a set of oscillators with $\theta=h\nu/kT$.

The more familiar type of expansion of the solution of (1.7) as a linear combination of orthogonal polynomials is presented for completeness in Appendix I.

3. MOMENTS OF THE LEVEL OCCUPATION DISTRIBUTION

We define the factorial moments of $x_n(t)$ by

$$f_m(t)=\sum_{n=0}^{\infty} n(n-1)\cdots(n-m+1)x_n(t) \qquad m=1,\,2,\,\cdots \tag{3.1a}$$

$$f_0(t)=\sum_{n=0}^{\infty} x_n(t)=1. \tag{3.1b}$$

Clearly the internal energy of our system is

$$E(t)=h\nu\sum nx_n(t)=h\nu f_1(t). \tag{3.2}$$

In general

$$f_m(t)=\frac{\partial^m}{\partial z^m}G(z,t)\bigg]_{z=1}. \tag{3.3}$$

A differential equation for f_m is readily derivable from (2.2), which we write as

$$\frac{1}{\kappa}\frac{\partial G}{\partial t}=(z-1)e^{-\theta}F \tag{3.4}$$

with

$$F=\frac{\partial G}{\partial z}[(z-1)+(1-e^{\theta})]+G. \tag{3.5}$$

Then by differentiating (3.4) m times with respect to z and setting $z=1$ we find

$$\frac{1}{\kappa}\frac{\partial f_m}{\partial t}=me^{-\theta}\frac{\partial^{m-1}F}{\partial z^{m-1}}\bigg]_{z=1}.$$

But (3.5) yields

$$\frac{\partial^{m-1}F}{\partial z^{m-1}}\bigg]_{z=1}=m\frac{\partial^{m-1}G}{\partial z^{m-1}}\bigg]_{z=1}+(1-e^{\theta})\frac{\partial^{m}G}{\partial z^{m}}\bigg]_{z=1}. \tag{3.6}$$

Hence

$$\frac{1}{\kappa}\frac{df_m}{dt}+m(1-e^{-\theta})f_m=m^2e^{-\theta}f_{m-1}. \tag{3.7}$$

By using the steady state value of f_1

$$\begin{aligned} f_1(\infty)&=\sum_{n=0}^{\infty} ne^{-n\theta}(1-e^{-\theta}) \\ &=e^{-\theta}/(1-e^{-\theta}) \end{aligned} \tag{3.8}$$

(3.7) is equivalent to

$$\frac{df_m}{d\tau}+mf_m=m^2f_{m-1}f_1(\infty) \tag{3.9}$$

and

$$f_m(\tau)=f_m(0)e^{-m\tau}+m^2f_1(\infty)e^{-\tau m}\int_0^{\tau} f_{m-1}(x)e^{mx}dx. \tag{3.10}$$

Since by (3.1b) $f_0(t)=1$ we find

$$f_1(t)=f_1(0)e^{-\tau}+f_1(\infty)(1-e^{-\tau}). \tag{3.11}$$

The variation of the internal energy with time is obtained by combining (3.2) with (3.11)

$$\frac{E(t)-E(\infty)}{E(0)-E(\infty)}=e^{-\tau} \tag{3.12}$$

as has been previously obtained by Bethe and Teller.[11]

Substitution of (3.11) into (3.10) when $m=2$ yields

$$\begin{aligned} f_2(t)=&2f_1^2(\infty)+4f_1(\infty)[f_1(0)-f_1(\infty)]e^{-\tau} \\ &+[f_2(0)-4f_1(0)f_1(\infty)+2f_1^2(\infty)]e^{-2\tau}. \end{aligned} \tag{3.13}$$

The dependence of the dispersion of our distribution on time is given by

$$\begin{aligned} \sigma^2(t)&=\langle(n-f_1)^2\rangle_{\mathrm{Av}}=f_2+f_1(1-f_1) \\ &=\sigma^2(\infty)+[\sigma^2(0)-\sigma^2(\infty)]e^{-2\tau} \\ &\quad+[f_1(0)-f_1(\infty)][1+2f_1(\infty)]e^{-\tau}(1-e^{-\tau}) \end{aligned} \tag{3.14}$$

where

$$\sigma^2(\infty)=f_1(\infty)[1+f_1(\infty)]. \tag{3.14a}$$

4. THE RELAXATION OF ONE BOLTZMANN DISTRIBUTION TO ANOTHER

It will now be shown that if our oscillators are initially distributed in their energy levels according to some Boltzmann distribution, then this distribution will persist during the relaxation but its effective temperature will vary monotonically until the temperature of the heat bath is achieved.

Let

$$x_n(0)=(1-e^{-\Theta_0})e^{-n\Theta_0} \tag{4.1}$$

where $\theta_0=h\nu/kT_0$, T_0 being the temperature corresponding to the initial distribution. Then

$$G_0(z)=\sum z^n x_n(0)=(1-e^{-\theta_0})/(1-ze^{-\theta_0}). \tag{4.2}$$

Hence, (2.13) yields

$$G(z,t)=\frac{(1-e^{\theta})(1-e^{-\theta_0})}{[(e^{-\tau}-e^{\theta})+e^{(\theta-\theta_0)}(1-e^{-\tau})]+z[(1-e^{-\tau})-e^{-\theta_0}(1-e^{\theta-\tau})]} \tag{4.3}$$

so that

$$x_n(t)=[1-\exp(-\Theta)]\exp(-n\Theta) \tag{4.4a}$$

where

$$\Theta=\log\left\{\frac{e^{-\tau}(1-e^{\theta-\theta_0})-e^{\theta}(1-e^{-\theta_0})}{e^{-\tau}(1-e^{\theta-\theta_0})-(1-e^{-\theta_0})}\right\} \tag{4.4b}$$

and τ is given by (2.12), $\tau=\kappa t[1-\exp(-\theta)]$.

Our distribution (4.4) is that of Boltzmann at all times and the "effective temperature" $\mathcal{T}$ varies with time as $\mathcal{T}=h\nu/k\Theta(\tau)$. We have plotted $1/\Theta$ as a function of time for various initial and final temperatures in Fig. 1.

5. INITIAL POISSON DISTRIBUTION

We now examine the relaxation of the Poisson distribution

$$x_n(0)=e^{-a}a^n/n! \tag{5.1}$$

where a is the mean value of n. We have

$$G_0(z)=\sum_{n=0}^{\infty} z^n x_n(0)=e^{-a(1-z)} \tag{5.2}$$

so that by (3.3)

$$f_1(0)=\bar{n}=\partial G_0/\partial z=a \tag{5.3a}$$

and

$$\sigma^2=\langle(n-\bar{n})^2\rangle_{\text{Av}}=a. \tag{5.3b}$$

Application of (2.13) yields

$$G(z,t)=\frac{1-e^{\theta}}{(z-e^{\theta})-(z-1)e^{-\tau}} \times\exp\left\{-\frac{ae^{-\tau}(1-z)(1-e^{\theta})}{(z-e^{\theta})-(z-1)e^{-\tau}}\right\}. \tag{5.4}$$

Since the generating function of Laguerre polynomials defined by[14]

$$n!L_n(y)=e^{y}(d/dy)^n(e^{-y}y^n)$$

$$=n!\sum_{\nu=0}^{n}\binom{n}{n-\nu}\frac{(-y)^{\nu}}{\nu!} \tag{5.5a}$$

is

$$(1-\alpha)^{-1}\exp\{y\alpha/(\alpha-1)\}=\sum_{n=0}^{\infty}\alpha^n L_n(y) \tag{5.5b}$$

we obtain

$$x_n(t)=\left[\frac{1-e^{\theta}}{e^{-\tau}-e^{\theta}}\right]\left[\exp\left\{\frac{ae^{-\tau}(e^{\theta}-1)}{e^{-\tau}-e^{\theta}}\right\}\right]\left[\frac{1-e^{-\tau}}{e^{\theta}-e^{-\tau}}\right]^n \times L_n\left\{\frac{ae^{-\tau}(e^{\theta}-1)^2}{(1-e^{-\tau})(e^{-\tau}-e^{\theta})}\right\}. \tag{5.6}$$

Since $L_n(0)=1$ it is easy to show that as $\tau\rightarrow\infty$, $x_n(t)$ tends to the final equilibrium Boltzmann distribution (2.14b). We have plotted $x_n(t)$ in Fig. 2 for $\theta=3$ and $a=15$.

6. ALL MOLECULES INITIALLY IN *m*TH STATE

Let

$$x_n(0)=\begin{cases}1 & \text{if } n=m\\ 0 & \text{otherwise.}\end{cases} \tag{6.1}$$

This sharp distribution broadens and its peak is displaced toward $n=0$ with increasing time. Then

$$G_0(z)=z^m \tag{6.2}$$

and

$$\begin{aligned}G(z,t)&=\frac{(1-e^{\theta})[z(1-e^{-\tau+\theta})-e^{\theta}(1-e^{-\tau})]^m}{[z(1-e^{-\tau})+(e^{-\tau}-e^{\theta})]^{m+1}}\\&=\frac{(1-e^{\theta})e^{m\theta}(e^{-\tau}-1)^m[1-\alpha z]^m}{(e^{-\tau}-e^{\theta})^{m+1}[1-\beta z]^{m+1}}\end{aligned} \tag{6.3}$$

where

$$\alpha=\left(\frac{e^{-\tau}-e^{-\theta}}{e^{-\tau}-1}\right) \quad\text{and}\quad \beta=\left(\frac{e^{-\tau}-1}{e^{-\tau}-e^{\theta}}\right). \tag{6.4}$$

Now, it is well known[15] that if $|y|<1$ and $|y(1-s)|<1$

$$(1-y)^{a-1}(1-y+sy)^{-a}=\sum_{n=0}^{\infty} y^n F(-n,a,1;s) \tag{6.5}$$

F being the hypergeometric function. Hence if we let $a=-m$

$$\begin{aligned}x_n(t)&=\frac{(1-e^{\theta})e^{m\theta}}{(e^{-\tau}-e^{\theta})}\left(\frac{e^{-\tau}-1}{e^{-\tau}-e^{\theta}}\right)^{m+n}F(-n,-m,1;u^2)\\u&=\frac{\sinh\frac{1}{2}\theta}{\sinh\frac{1}{2}\tau}.\end{aligned} \tag{6.5a}$$

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[14] G. Szego, *Orthogonal Polynomials* (American Mathematical Society, 1939), p. 96.

[15] Erdelyi, Magnus, Oberhettinger, and Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 82.

A standard transformation formula yields

$$x_n(t)=\frac{(1-e^{\theta})e^{m\theta}}{(e^{-\tau}-e^{\theta})}\left(\frac{e^{-\tau}-1}{e^{-\tau}-e^{\theta}}\right)^{m+n}$$
$$\times[1-u^2]^{1+m+n}F(1+n,\,1+m,\,1;\,u^2). \quad (6.5b)$$

Note that as $\tau\to\infty$ (t large), $u\to0$ and $F\to1$ and the Boltzmann distribution develops as is required. When $\tau>\theta$, (6.5b) converges rapidly and is suitable for making calculations.

At early times we expect the distribution to be close to a Gaussian,

$$x_n(t)\simeq\frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}}\exp(n-\bar{n})^2/2\sigma^2. \quad (6.6)$$

Initially $\bar{n}(0)=m$ and $\sigma^2(0)=0$. Hence from (3.11) and (3.14)

$$\bar{n}(\tau)=f_1(t)=me^{-\tau}+f_1(\infty)(1-e^{-\tau}) \quad (6.7a)$$

$$\sigma^2(\tau)=\sigma^2(\infty)[1-e^{-2\tau}]$$
$$+[m-f_1(\infty)][1+2f_1(\infty)]e^{-\tau}(1-e^{-\tau}) \quad (6.7b)$$

where

$$\sigma^2(\infty)=f_1(\infty)[1+f_1(\infty)]$$

and

$$f_1(\infty)=e^{-\theta}(1-e^{-\theta})^{-1}.$$

It is to be noted that the relaxation from any initial distribution can be expressed as a linear combination of the $x_n(t)$'s which result from initially sharp distributions.

APPENDIX I. FOURIER SERIES SOLUTION OF EQ. (1.7)

For completeness we shall discuss the solution of (1.7) as a linear combination of a certain set of eigenfunctions. This form of solution could be used as the basis of a perturbation theory or for the analysis of complicated initial distributions for which $G_0(z)=G(z,0)$ [see Eq. (2.1)] cannot be summed easily.

We seek solutions $x_n(t)$ which are a superposition of terms of the following type

$$a_\mu l_n(\mu)\exp\{-\mu t\kappa(1-e^{-\theta})\}=a_\mu l_n(\mu)e^{-\mu\tau}, \quad (I.1)$$

where μ is a positive number and a_μ a constant which is to be determined from the initial level population distribution $\{x_n(0)\}$. Direct substitution of (I.1) into (1.7) yields a difference equation in the numbers $\{l_n(\mu)\}$

$$(e^{-\theta}-1)\mu l_n=ne^{-\theta}l_{n-1}$$
$$-\{n+(n+1)e^{-\theta}\}l_n+(n+1)l_{n+1}$$
$$n=0,\,1,\,2,\,\cdots. \quad (I.2)$$

This set of equations can be solved through the introduction of the generating function

$$F(w,\mu)=\sum_{n=0}^{\infty}l_n(\mu)w^n. \quad (I.3a)$$

Multiplication of (I.2) by w^n and summation with respect to n yields, after application of (I.3a) and

$$w\frac{\partial F}{\partial w}=\sum_{n=0}^{\infty}nl_n(\mu)w^n, \quad (I.3b)$$

$$F'(w)/F(w)=\mu(w-1)^{-1}-(\mu+1)(w-e^{\theta})^{-1} \quad (I.4)$$

whose solution is

$$F(w,\mu)=(1-w)^{\mu}(1-we^{-\theta})^{-\mu-1} \quad (I.5)$$

if l_0 is chosen to be 1. Our required functions $l_n(\mu)$ are the coefficients of w^n in $F(w,\mu)$. These functions have been studied by Gottlieb and can be shown to be[16]

$$l_n(\mu)=e^{\theta\mu}\Delta^n\left\{\binom{\mu}{n}e^{-\theta\mu}\right\} \quad (I.6a)$$

or

$$l_n(\mu)=e^{-n\theta}\sum_{\nu=0}^{\infty}(1-e^{\theta})^{\nu}\binom{n}{\nu}\binom{\mu}{\nu} \quad (I.6b)$$

where the standard binomial coefficient notation is used with

$$\binom{n}{\nu}=\begin{cases}n!/\nu!(n-\nu)! & \text{if}\quad n\geqslant\nu\\ 0 & \text{if}\quad n<\nu\quad\text{or}\quad\nu<0\\ 1 & \text{if}\quad\nu=0.\end{cases} \quad (I.7)$$

The first few of these functions are

$$l_n(0)=e^{-n\theta} \quad (I.8a)$$

$$l_n(1)=e^{-n\theta}\{1+(1-e^{\theta})n\}. \quad (I.8b)$$

These functions can be written in various ways in terms of hypergeometric functions; for example[17]

$$l_n(\mu)=F(-n,\,\mu+1,\,1;\,1-e^{-\theta}). \quad (I.9)$$

If μ is chosen to be an integer, it is clear by symmetry from (I.6b) that

$$e^{n\theta}l_n(\mu)=e^{\mu\theta}l_\mu(n). \quad (I.10)$$

A pair of useful orthogonality relations exist when μ and n are non-negative integers

$$\sum_{\nu=0}^{\infty}e^{-\theta\nu}l_n(\nu)l_m(\nu)=\begin{cases}0 & n\neq m\\ e^{-n\theta}(1-e^{-\theta})^{-1} & n=m\end{cases} \quad (I.11a)$$

$$\sum_{n=0}^{\infty}e^{n\theta}l_n(\nu)l_n(\mu)=\begin{cases}0 & \mu\neq\nu\\ e^{\nu\theta}(1-e^{-\theta})^{-1} & \mu=\nu.\end{cases} \quad (I.11b)$$

Gottlieb has also shown that for a fixed complex number x and large n

$$l_n(x)=(-1)^n(1-e^{-\theta})^{-x-1}\binom{x}{n}+O(n^{-Rex-2}). \quad (I.12)$$

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[16] M. J. Gottlieb, Am. J. Math. **60**, 455 (1938).

[17] Erdelyi, Magnus, Oberhettinger, and Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, p. 225.

Hence as $n \to \infty$, $l_n(x) \to 0$. This shows that our $l_n(x)$'s satisfy the physical requirement that the population of states characterized by the quantum number n decreases as $n \to \infty$ for θ fixed.

We can now construct a general solution of (1.7) by superposition of terms (I.1),

$$x_n(t) = \sum_{\mu=0}^{\infty} a_\mu l_n(\mu) e^{-\mu\tau} \tag{I.13a}$$

$$= \sum_{\mu=0}^{\infty} a_\mu e^{\theta(\mu-n)} l_\mu(n) e^{-\mu\tau} \tag{I.13b}$$

where the constants a_μ are determined in the usual manner through the orthogonality relations. We find

$$a_\mu = (1-e^{-\theta}) \sum_{n=0}^{\infty} x_n(0) l_\mu(n) \tag{I.14a}$$

or alternatively

$$a_\mu = (1-e^{-\theta}) e^{-\mu\theta} \sum_{n=0}^{\infty} e^{n\theta} l_n(\mu) x_n(0). \tag{I.14b}$$

When $x_n(0)$ is chosen to be a Boltzmann distribution, one can by repeated use of the generating function $F(w,\mu)$ of (I.5) readily obtain Eq. (4.4) for $x_n(t)$.

Rubin and Shuler[6] previously derived the following formula for $x(n,t) = x_n(t)$ which is to be valid when θ is very small; ($L_n(x)$ is the nth Laguerre polynomial)

$$x(n,t) = e^{-n\theta} \sum_{\mu=0}^{\infty} a_\mu L_\mu(n\theta) \exp(-\mu\theta t k_{10}) \tag{I.15a}$$

where

$$a_\mu = \theta \int_0^\infty x(y,0) L_\mu(\theta y) dy. \tag{I.15b}$$

This result can be obtained from (I.14a) and (I.13b) by letting $\theta \to 0$ in certain terms and retaining it in others. Gottlieb pointed out that

$$\lim_{\theta\to 0} l_n(x/\theta, \theta) = L_n(x). \tag{I.16}$$

If we write $l_\mu(n) = l_\mu(n\theta/\theta, \theta)$ and suppose $n\theta$ is fixed while $\theta \to 0$, and if we let $1-\exp(-\theta) \simeq \theta$, (I.14a) becomes

$$a_\mu \simeq \theta \sum_{y=0}^{\infty} x(y,0) L_\mu(y\theta) \simeq \theta \int_0^\infty x(y,0) L_\mu(\theta y) dy.$$

The conversion of the summation to an integration is valid if $x(y,0)$ and $L_\mu(\theta y)$ are slowly varying functions of y. Equation (I.13b) reduces to (I.15a) if one uses (I.16), sets $\exp\theta\mu = 1$ and writes $\tau = tk_{10}(1-e^{-\theta}) \simeq k_{10}\theta t$.

APPENDIX II. THE RELAXATION EQUATION FOR VIBRATIONAL-TRANSLATIONAL ENERGY EXCHANGE

We now wish to derive the analog of the relaxation equation (1.6) when the energy exchange is between the vibration of the harmonic oscillators and the translational degrees of freedom of the heat bath molecules. The formulation presented here is in principle analogous to that given by Rubin and Shuler[6] but is more detailed in that it takes explicit account of the matrix elements for the transitions between the translational "energy levels."

Let

$x_n(t)$ = fraction of excited oscillators in vibrational level n
y_i = concentration of heat bath molecules (or atoms) with momentum† p_i
$P_{n,\,n+1;\,i,\,i-1}$ = joint probability per collision for the energy transfer $nh\nu \to (n+1)h\nu$ as $p_i \to p_{i-1}$.

The relaxation equation can now be written as [see (1.2)]

$$\begin{aligned}\frac{dx_n(t)}{dt} = -Z\Big[x_n\Big(\sum_{i=0}^{\infty} y_i P_{n,\,n+1;\,i,\,i-1} &+ \sum_{i=0}^{\infty} y_i P_{n,\,n-1;\,i,\,i+1}\Big) \\ &- x_{n+1} \sum_{i=0}^{\infty} y_i P_{n+1,\,n;\,i,\,i+1} \\ &- x_{n-1} \sum_{i=0}^{\infty} y_i P_{n-1,\,n;\,i-1}\Big]\end{aligned} \tag{II.1}$$

where Z is again the collision number. The joint transition probabilities can now be written as

$$\begin{aligned} P_{n,\,n+1;\,i,\,i-1} &= P_{10}(n+1) Q_{i(-)} \\ P_{n,\,n-1;\,i,\,i+1} &= P_{10} n Q_{i(+)} \end{aligned} \tag{II.2}$$

where $(n+1)P_{10}$ and nP_{10} are the vibrational transition probabilities (see 1.1) and where the Q's are the translational transition probabilities to be determined. Substitution of (II.2) in (II.1) leads to

$$\begin{aligned}\frac{dx_n(t)}{dt} = ZP_{10}(n+1) &\times\Big[x_{n+1} \sum_i y_i Q_{i(+)} - x_n \sum_i y_i Q_{i(-)}\Big] \\ &+ ZP_{10} n\Big[x_{n-1} \sum_i y_i Q_{i(-)} - x_n \sum_i y_i Q_{i(+)}\Big].\end{aligned} \tag{II.3}$$

At equilibrium, (i.e., as $t \to \infty$), we have

$$\begin{aligned}\frac{dx_n(\infty)}{dt} &= 0 \\ \frac{x_{n+1}(\infty)}{x_n(\infty)} = \frac{x_n(\infty)}{x_{n-1}(\infty)} &= e^{-\theta}\end{aligned} \tag{II.4}$$

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† The indices i, $i \pm 1$ do not represent successive translational energy levels but are used to indicate translational levels separated by $h\nu$.

and Eq. (II.3) becomes

$$0=ZP_{10}(n+1)x_n(\infty)\Big[e^{-\theta}\sum_i y_iQ_{i(+)}-\sum_i y_iQ_{i(-)}\Big]$$
$$-ZP_{10}nx_{n-1}(\infty)\Big[e^{-\theta}\sum_i y_iQ_{i(+)}-\sum_i y_iQ_{i(-)}\Big]. \tag{II.5}$$

Since the heat bath is assumed to remain at its Maxwell-Boltzmann equilibrium distribution at all times t, $y_i\neq f(t)$ and $y_i(\infty)=y_i$.

The first two terms in Eq. (II.5) refer to the rate of the (vibrational) transition $n\rightleftarrows n+1$ and the last two terms to the rate of the transition $n\rightleftarrows n-1$. By the principle of detailed balancing at equilibrium, the net rate of each of these transitions must be independently zero to satisfy (II.5). We thus find that

$$\sum_i y_iQ_{i(-)}=e^{-\theta}\sum_i y_iQ_{i(+)}. \tag{II.5a}$$

Substitution of (II.5a) into (II.3) leads to

$$\frac{dx_n(t)}{dt}=ZP_{10}\sum_i y_iQ_{i(+)}\{ne^{-\theta}x_{n-1}$$
$$-[n+(n+1)e^{-\theta}]x_n+(n+1)x_{n+1}\} \tag{II.6}$$

which is of the same form as (1.6) except for the replacement of $k_{10}(1-e^{-\theta})^{-1}$ by $ZP_{10}\sum_i y_iQ_{i(+)}$. To evaluate the term in front of the braces in (II.6) we write, with Landau and Teller[4]

$$y_i=y_w=2N(m/2kT)^2w^3\exp\left(-\frac{mw^2}{2kT}\right) \tag{II.7}$$

for the number of heat bath molecules with momentum mw undergoing collisions (N is the total number of heat bath molecules) and

$$Q_{i(+)}=Q_{w(+)}=Q_0e^{-2\pi\nu a/w} \tag{II.8}$$

where Q_0 is a constant, ν is the frequency of the oscillator, and where a is a length characteristic of the interaction forces in the collisions between the oscillators and the heat bath molecules. Replacing the summation over i indicated in (II.6) by integration over the velocities w one obtains

$$\frac{dx_n(t)}{dt}=k_{10}Q_0\left(\frac{6}{\pi}\frac{kT}{\epsilon}\right)^{-\frac{1}{2}}\exp\left[-\frac{3}{2}\left(\frac{\epsilon}{kT}\right)^{\frac{1}{3}}\right]$$
$$\times\{ne^{-\theta}x_{n-1}-[n+(n+1)e^{-\theta}]x_n$$
$$+(n+1)x_{n+1}\} \tag{II.9}$$

where $k_{10}=ZNP_{10}$ has been defined in connection with (1.6) and where $\epsilon=m(2\pi\nu a)^2$ with m equal to the effective mass of the collision system. One thus obtains finally

$$\frac{dx_n(t)}{dt}=k_{10}'\{ne^{-\theta}x_{n-1}$$
$$-[n+(n+1)e^{-\theta}]x_n+(n+1)x_{n+1}\} \tag{II.9a}$$

where

$$k_{10}'=k_{10}Q_0\left(\frac{6}{\pi}\frac{kT}{\epsilon}\right)^{-\frac{1}{2}}\exp\left[-\frac{3}{2}\left(\frac{\epsilon}{kT}\right)^{\frac{1}{3}}\right] \tag{II.9b}$$

is the transition probability used in (1.7a) for the vibration-translation energy exchange.

A more accurate evaluation of the joint vibrational-translational transition probabilities in (II.2) could be obtained from the quantum mechanical treatments of Jackson and Mott[18] and Herzfeld and his co-workers.[19]

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[18] T. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) **A137**, 703 (1932).

[19] Slawsky, Schwartz, and Herzfeld, J. Chem. Phys. **20**, 1591 (1952); R. N. Schwartz and K. F. Herzfeld, *ibid.*, 22, 767 (1954); see also K. F. Herzfeld in *Thermodynamics and Physics of Matter* (Princeton University Press, Princeton, 1955), Sec. H.