Journal of Statistical Physics, Vol. 11, No. 1, 1974

Decay of Correlations in Vibrational Relaxation

Joanna I. Scott[1] and Irwin Oppenheim[1]

Received January 14, 1974

We investigate the decay of initial vibrational correlations in a dilute gas mixture of diatomic molecules and structureless particles. We use the techniques of Davis and Oppenheim to derive an equation for vibrational relaxation which is suitable for correlated systems. We then use the Landau–Teller transition probabilities and solve for the one- and two-molecule distribution functions and the two-molecule correlation functions. We find that the correlations decay faster than the distribution functions, which agrees with the results of Oppenheim, Shuler, *et al.* for other systems.

KEY WORDS: Vibrational correlations; dynamics of correlations; vibrational relaxation; master equation.

1. INTRODUCTION

The decay of initial correlations has been studied in a number of model systems which can be treated analytically in complete detail.⁽¹⁻⁴⁾ Here we study vibrational relaxation in a dilute, isotropic gas of diatomic molecules and atoms with initial vibrational correlations. This system is the dynamical analog of a system treated previously from a stochastic viewpoint.

Unfortunately, we know of no experimental method which will produce vibrational correlations in the system studied here; the vibrational density matrix appears to be a product of single-molecule density matrices for any physically realizable system. The crucial factor is that the vibrational density matrix does not depend on the positions of the molecules. Vibrational

---

Supported in part by the National Science Foundation.

[1] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

correlations can and do exist between individual molecules. After a collision the molecules will be correlated for at least a mean free time. There are also unusual circumstances$^{(5)}$ for which the molecular chaos assumption is invalid and molecules can be correlated before a collision, but only if they have collided in the past. These types of correlations will appear in the complete density matrix for the molecules, but to obtain the vibrational part of the density matrix, one integrates over the positions of the molecules and the correlations disappear; the probability that two molecules selected at random from a large system are correlated is negligible. It appears probable to us that, in order to have correlations in any system, either the density matrix under investigation must depend on the positions of the particles or the particles must be fixed in a lattice.

In spite of the apparent impossibility of constructing correlated initial conditions for vibrational relaxation, we feel that the problem is worth studying as a model system. If we assume a correlated initial condition, we can derive a hierarchy of equations analogous to the BBGKY hierarchy. The main distinction is that the distribution functions in the BBGKY equations depend on the positions of the particles and correlations certainly can exist. Bogoliubov's$^{(6)}$ hypothesis that the n-particle distribution functions become time-independent functionals of the single-particle distribution functions after an initial short time interval has been used extensively to derive kinetic equations and generalized Boltzmann equations for dense systems. The validity of this hypothesis has been investigated by Green and Piccirelli,$^{(7)}$ and found to be at least partially true, but further investigation of the limits of applicability is needed. It is of interest to investigate the hierarchy of equations for vibrational relaxation and to determine how well Bogoliubov's hypothesis applies to correlated n-molecule vibrational distribution functions.

We first derive the hierarchy of relaxation equations for the reduced vibrational density matrices. We follow closely the methods Davis and Oppenheim$^{(5,8)}$ used to derive the vibrational master equation, but with important differences. They assumed that the vibrational distribution functions were uncorrelated at all times and they used the molecular chaos assumption. We assume that the vibrational distribution functions do not factor initially and we do not use the molecular chaos assumption. The resulting equations are valid for correlated systems and reduce to the Davis and Oppenheim result when the correlations vanish.

The procedures we and Davis and Oppenheim use are based on the projection operator technique of Zwanzig,$^{(9)}$ a derivation of the classical Boltzmann equation by Mazur and Biel,$^{(10)}$ and the Wigner function approach to statistical mechanics.$^{(11)}$

In later sections we study the decay of initial correlations, using the equations we have derived. We use the superposition principle to obtain closed equations for the one- and two-molecule distribution functions. We assume that the molecules are harmonic oscillators and use the Landau–Teller transition probabilities. We solve the resulting equations and compare the decay of the one- and two-molecule distribution functions with that of the two-molecule correlation function.

2. THE EXACT *N*-BODY EQUATIONS

The system of interest here is a dilute, isotropic gas consisting of N_M diatomic molecules and N_A structureless particles (atoms) in a volume V. The total number of particles is $N = N_M + N_A$.

We follow closely the procedures used by Davis and Oppenheim$^{(8)}$ to derive the vibrational master equation and we will discuss only the points where our derivation differs significantly from theirs.

We define the Wigner operators $\hat{F}^N(R^N, P^N, t)$, the Hamiltonian $H = H_0{}^N(CM) + H_0^{N_M}(\text{int}) + U^N$, the Liouville operator $\hat{L}^N = L_0{}^N(CM) + \hat{L}_0^{N_M}(\text{int}) + \hat{\theta}^N$, and the reduced Wigner operators $\hat{F}^n(R^n, P^n, t)$ in the same manner as in Ref. 8 except for obvious differences caused by the presence of atoms in our system. We transform the reduced Wigner operators to a "rotating" frame:

$$\hat{F}^{*n}(R^n, P^n, t) = [\exp(i\hat{L}_0{}^n t)]\hat{F}^n(R^n, P^n, t) \tag{1}$$

where $\hat{L}_0{}^n = \hat{L}_0{}^n(\text{CM}) + \hat{L}_0{}^n(\text{int})$, and $\hat{F}^{*n}$ is the Wigner operator in the "rotating" frame.

Our basic equation follows fairly easily from the Schrödinger equation in the thermodynamic limit:

$$\begin{aligned}\frac{\partial\hat{F}^{*n}}{\partial t}&(R^n, P^n, t)\\ &= -i[\exp(i\hat{L}_0{}^n t)]\hat{\theta}^n[\exp(-i\hat{L}_0{}^n t)]\hat{F}^{*n}\\ &\quad-\frac{iN_M}{V}[\exp(i\hat{L}_0{}^n t)]\sum_{j=1}^{n}\mathscr{L}_{M_jM_{n+1}}[\exp(-i\hat{L}_{0,M}^{n+1}t)]\hat{F}_M^{*n+1}\\ &\quad-\frac{iN_A}{V}[\exp(i\hat{L}_0{}^n t)]\sum_{j=1}^{n}\mathscr{L}_{M_jA_{n+1}}[\exp(-i\hat{L}_{0,A}^{n+1}t)]\hat{F}_A^{*n+1}\end{aligned} \tag{2}$$

where

$$\mathscr{L}_{M_jM_{n+1}}\hat{F}_M^{n+1} = \sum_{z_{n+1}}\int d\mathbf{R}_{n+1}\,d\mathbf{P}_{n+1}\,\langle z_{n+1}|\hat{\theta}^2_{M_jM_{n+1}}\hat{F}_M^{n+1}|z_{n+1}\rangle \tag{3a}$$

$$\mathscr{L}_{M_jA_{n+1}}\hat{F}_A^{n+1} = \int d\mathbf{R}_{n+1}\,d\mathbf{P}_{n+1}\,\hat{\theta}^2_{M_jA_{n+1}}\hat{F}_A^{n+1} \tag{3b}$$

Here $\hat{F}_M^{n+1}$ and $\hat{F}_A^{n+1}$ designate $(n + 1)$-particle Wigner operators where the first n particles are molecules and the last particle is a molecule (M) or atom (A), respectively. Similarly, the subscripts M and A on $\mathscr{L}$ and $\hat{\theta}^2$ indicate what types of particles are interacting.

3. REARRANGEMENT OF THE MANY-BODY PROBLEM

We are not interested in all of $\hat{F}^n$, but only in the vibrational part of the density matrix, $\rho^n_{\text{vib}}(t)$:

$$\begin{aligned}&\langle v^n|\rho^n_{\text{vib}}(t)|\bar{v}^n\rangle \\ &\quad = (1/V^n)\int dR^n\, dP^n \sum_{j^n m^n} \langle j^n m^n v^n|\hat{F}^n(R^n, P^n, t)|j^n m^n \bar{v}^n\rangle\end{aligned} \tag{4}$$

The vibrational distribution function $P^n(t)$ is the diagonal part of $\rho^n_{\text{vib}}(t)$:

$$P^n_{v^n}(t) = \langle v^n|\rho^n_{\text{vib}}(t)|v^n\rangle \tag{5}$$

We now define two projection operators D^n and $\mathscr{P}^n$. For an arbitrary operator χ^n

$$\langle z^n|D^n\chi^n|\bar{z}^n\rangle \equiv \langle z^n|\chi^n|\bar{z}^n\rangle\, \Delta(\varepsilon_z{}^n, \varepsilon_{\bar{z}}{}^n) \tag{6}$$

where $\varepsilon_z{}^n$ is the energy of the internal state $|z^n\rangle$; D^n discards all matrix elements with different initial and final internal energies. This is not the same definition that is used by Davis and Oppenheim(8): Their operator D selects diagonal elements, rather than energetically diagonal elements. The projector $\mathscr{P}^n$ is defined by

$$\mathscr{P}^n \equiv \mu^n \mathscr{T}^n D^n \tag{7}$$

where

$$\mu^n \equiv \hat{g}^n \hat{\phi}^n(P^n) \mathscr{J}^n_{J^n} \tag{8}$$

$$\mathscr{T}^n \equiv (1/V^n)\int dR^n\, dP^n\, \text{Tr}^n_{\text{rot}} \tag{9}$$

The functions $\hat{g}^n$, $\hat{\phi}^n(P^n)$, and $\mathscr{J}^n_{J^n}$ are defined in Ref. 8. $\mathscr{P}^n$ differs from the projection operator given in Ref. 8 since the operators D^n are different, but the properties given for $\mathscr{P}^n$ are still valid. In particular,

$$\mathscr{P}^n L_0{}^n(\text{int}) = 0 \tag{10}$$

since $L_0{}^n(\text{int})$ has no energetically diagonal elements.

We now derive two equations by applying $\mathscr{P}^n$ and $(1 - \mathscr{P}^n)$ to Eq. (2) and use the properties of D^n and $\mathscr{P}^n$ to simplify the results. We obtain

$$\frac{\partial f^n}{\partial t} = i\frac{N_M}{V}\mathscr{P}^n \sum_{j=1}^{n} \mathscr{L}_{M_j M_{n+1}}[\exp(-iL^{n+1}_{0,M}t)]f^{n+1}_M$$

$$
\begin{aligned}
&-\frac{iN_A}{V}\mathscr{P}^n \sum_{j=1}^{n} \mathscr{L}_{M_jA_{n+1}}[\exp(-iL_{0,A}^{n+1}t)]f_A^{n+1} \\
&-i\frac{N_M}{V}\mathscr{P}^n \sum_{j=1}^{n} \mathscr{L}_{M_jM_{n+1}}[\exp(-iL_{0,M}^{n+1}t)]h_M^{n+1} \\
&-i\frac{N_A}{V}\mathscr{P}^n \sum_{j=1}^{n} \mathscr{L}_{M_jA_{n+1}}[\exp(-iL_{0,A}^{n+1}t)]h_A^{n+1}
\end{aligned}
\tag{11}
$$

$$
\begin{aligned}
\frac{\partial h^n}{\partial t} = &-i[\exp(iL_0{}^nt)]\theta^n[\exp(-iL_0{}^nt)]h^n \\
&-i[\exp(iL_0{}^nt)]\theta^n[\exp(-iL_0{}^nt)]f^n \\
&-i\frac{N_M}{V}(1-\mathscr{P}^n)[\exp(iL_0{}^nt)]\sum_{j=1}^{n}\mathscr{L}_{M_jM_{n+1}}\hat{F}_M^{n+1} \\
&-i\frac{N_A}{V}(1-\mathscr{P}^n)[\exp(iL_0{}^nt)]\sum_{j=1}^{n}\mathscr{L}_{M_jA_{n+1}}\hat{F}_A^{n+1}
\end{aligned}
\tag{12}
$$

where we have defined

$$
f^n \equiv \mathscr{P}^n\hat{F}^{*n}, \qquad h^n \equiv (1-\mathscr{P}^n)\hat{F}^{*n}, \qquad \hat{F}^{*n} = f^n + h^n \tag{13}
$$

We now note that all the terms in Eq. (11) are of the form

$$
\begin{aligned}
&i\frac{N}{V}\mathscr{P}^n\mathscr{L}_{j,n+1}[\exp(-iL_0^{n+1}t)]\chi^{n+1} \\
&\qquad = i\frac{N}{V}\mu^nD^n\mathscr{T}^n\mathscr{L}_{j,n+1}[\exp(-iL_0^{n+1}t)]\chi^{n+1}
\end{aligned}
\tag{14}
$$

where χ^{n+1} is either f^{n+1} or h^{n+1} and we have ignored subscripts M and A. From the properties of $\mathscr{P}^n$ and D^n given in Ref. 8 and Eq. (10) we see that Eq. (14) can be written as

$$
\begin{aligned}
&i(N/V)\mu^nD^n\mathscr{T}^n\{\exp[-iL_0^{n-1}(\text{int})t]\} \\
&\quad \times \mathscr{L}_{j,n+1}[\exp(-iL_{0,j,n+1}^2t)]\chi^{n+1} \\
&\quad = i(N/V)\mu^nD^n\mathscr{T}_j\{\exp[+iL_{0,j}(\text{int})t]\} \\
&\qquad \times\mathscr{L}_{j,n+1}[\exp(-iL_{0,j,n+1}^2t)]\mathscr{T}^{n-1}\chi^{n+1}
\end{aligned}
\tag{15}
$$

where

$$
L_0^{n-1}(\text{int}) = \sum_{\substack{k\neq j\\1}}^{n} L_{0,k}(\text{int}) \qquad \text{and} \qquad \mathscr{T}^{n-1} = \prod_{\substack{k\neq j\\1}}^{n}\mathscr{T}_k
$$

If we consider matrix elements, Eq. (15) will be multiplied by a factor $\exp(i\omega_{v_jv_j'}t)$ arising from the factor $\exp[iL_{0,j}(\text{int})t]$, where

$$
\omega_{vv'} = (\varepsilon_v - \varepsilon_{v'})/\hbar \tag{16}
$$

We are interested only in macroscopic effects and are not interested in times less than t_f, the mean free time of the particles. The exponential $\exp(i\omega_{v_j v_{j'}} t)$ will oscillate rapidly and can be considered zero if

$$\omega_{v_j v_{j'}} t_f \gg 1 \tag{17}$$

For a more detailed analysis see Ref. 5 or 14. Vibrational levels are usually widely spaced in diatomic molecules and condition (17) holds for almost all diatomic molecules at normal densities. We will assume that Eq. (17) holds whenever $\omega_{v_j v_{j'}} \neq 0$. This implies that the rhs of Eq. (15) becomes

$$i \frac{N}{V} \mu^n D_j \mathscr{T}_j \mathscr{L}_{j,n+1} [\exp(-iL^2_{0,j,n+1} t)] D^{n-1} \mathscr{T}^{n-1} \chi^{n+1} \tag{18}$$

We can use this result to rewrite the terms in Eq. (11).

We now "solve" Eq. (11) for $h^{n+1}(t)$. The solution contains a propagator $G^{n+1}(t)$ which is defined as the solution to

$$\frac{dG^{n+1}}{dt} = -iL^{n+1} G^{n+1}, \qquad G^{n+1}(0) = 1 \tag{19}$$

i.e., $G^{n+1}(t) = \exp(-iL^{n+1} t)$. If we now substitute for h^{n+1} in Eq. (11) and use the property that

$$D^{n-1} \mathscr{T}^{n-1} \chi^{n+1} = \chi^2_{j,n+1} D^{n-1} \mathscr{T}^{n-1} \tag{20}$$

for $\chi^{n+1} = G^{n+1}(t), L^{n+1}, \exp(-iL_0^{n+1} t)$, or $\mathscr{P}^{n+1}$, then we obtain an equation for $f^n(t)$:

$$\frac{\partial f^n}{\partial t} = \left(\frac{\partial f^n}{\partial t}\right)^M + \left(\frac{\partial f^n}{\partial t}\right)^R + \left(\frac{\partial f^n}{\partial t}\right)^I \tag{21}$$

where

$$\begin{aligned}
\left(\frac{\partial f^n}{\partial t}\right)^M = & -i \frac{N_M}{V} \mu^n \sum_{j=1}^{n} D_j \mathscr{T}_j \mathscr{L}_{M_j M_{n+1}} [\exp(-iL^2_{0,j,n+1} t)] D^{n-1} \mathscr{T}^{n-1} f_M^{n+1}(t) \\
& - \frac{iN_M}{V} \mu^n \int_0^t ds \sum_{j=1}^{n} D_j \mathscr{T}_j \mathscr{L}_{M_j M_{n+1}} G^2_{j,n+1}(s) \\
& \times \theta^2_{j,n+1} \{\exp[-iL^2_{0,j,n+1}(t-s)]\} D^{n-1} \mathscr{T}^{n-1} f_M^{n+1}(t-s) \\
& -i \frac{N_A}{V} \mu^n \sum_{j=1}^{n} D_j \mathscr{T}_j \mathscr{L}_{M_j A_{n+1}} [\exp(-iL^2_{0,j,n+1} t)] D^{n-1} \mathscr{T}^{n-1} f_A^{n+1}(t) \\
& -i \frac{N_A}{V} \mu^n \int_0^t ds \sum_{j=1}^{n} D_j \mathscr{T}_j \mathscr{L}_{M_j A_{n+1}} G^2_{j,n+1}(s) \\
& \times \theta^2_{j,n+1} \{\exp[-iL^2_{0,j,n+1}(t-s)]\} D^{n-1} \mathscr{T}^{n-1} f_A^{n+1}(t-s)
\end{aligned} \tag{22}$$

$$
\begin{aligned}
\left(\frac{\partial f^n}{\partial t}\right)^R = & -i\frac{N_M}{V}\mu^n\int_0^t ds\sum_{j=1}^{n} D_j\mathcal{T}_j\mathcal{L}_{M_jM_{n+1}}G^2_{j,n+1}(s) \\
& \times (1 - \{\exp[-iL^2_{0,j,n+1}(t-s)]\}\mathcal{P}^2_{j,n+1})D^{n-1}\mathcal{T}^{n-1} \\
& \times \left\{\frac{N_M}{V}\sum_{k=1}^{n+1}\mathcal{L}_{M_kM_{n+2}}\hat{F}^{n+2}_{MM}(t-s) + \frac{N_A}{V}\sum_{k=1}^{n+1}\mathcal{L}_{M_kA_{n+2}}\hat{F}^{n+1}_{MA}(t-s)\right\} \\
& -i\frac{N_A}{V}\mu^n\int_0^t ds\sum_{j=1}^{n} D_j\mathcal{T}_j\mathcal{L}_{M_jA_{n+1}}G^2_{j,n+1}(s) \\
& \times (1 - \{\exp[-iL^2_{0,j,n+1}(t-s)]\}\mathcal{P}^2_{j,n+1})D^{n-1}\mathcal{T}^{n-1} \\
& \times \left\{\frac{N_M}{V}\left[\sum_{k=1}^{n}\mathcal{L}_{M_jM_{n+2}} + \mathcal{L}_{A_{n+1},M_{n+2}}\right]\hat{F}^{n+2}_{AM}(t-s)\right. \\
& \left. + \frac{N_A}{V}\left[\sum_{k=1}^{n}\mathcal{L}_{M_kA_{n+2}} + \mathcal{L}_{A_{n+1}A_{n+2}}\right]\hat{F}^{n+2}_{AA}(t-s\right\}
\end{aligned}
\tag{23}
$$

$$
\begin{aligned}
\left(\frac{\partial f^n}{\partial t}\right)^I = & -i\frac{N_M}{V}\mu^n\sum_{j=1}^{n} D_j\mathcal{T}_j\mathcal{L}_{M_jM_{n+1}}G^2_{j,n+1}(t)D^{n-1}\mathcal{T}^{n-1}h^{n+1}_M(0) \\
& -i\frac{N_A}{V}\mu^n\sum_{j=1}^{n} D_j\mathcal{T}_j\mathcal{L}_{M_jA_{n+1}}G^2_{j,n+1}(t)D^{n-1}\mathcal{T}^{n-1}h^{n+1}_A(0)
\end{aligned}
\tag{24}
$$

We will refer to $(\partial f^n/\partial t)_M$, $(\partial f^n/\partial t)^R$, and $(\partial f^n/\partial t)^I$ as the master term, the remainder term, and the initial value term, respectively. Equations (22)–(24) are still exact for pairwise additive interactions in the thermodynamic limit when

$$\omega_{\min} t_f \gg 1 \tag{25}$$

where $\omega_{\min}$ is the minimum vibrational frequency in the system.

4. THE DILUTE ISOTROPIC GAS

We will now make use of the assumption that the system is a dilute isotropic gas. The singlet Wigner operator $F^1(t)$ and ${}^0g^1$ will be independent of $\mathbf{R}$ in an isotropic gas and if t_c and t_f are the mean times of and between collisions, respectively, a dilute gas satisfies the condition

$$t_c/t_f \ll 1 \tag{26}$$

There are two types of processes involved in the vibrational relaxation of our system: T–V transitions, in which energy is exchanged between the translational and/or rotational and vibrational degrees of freedom, and V–V transitions, in which a vibrational quantum is transferred between the molecules. These processes give rise to two time scales: t_{VV}, which is the time required for the establishment of an approximate Boltzmann distribution of the vibrational energies, and t_{TV}, which is the time required for complete equilibration of the system. For most diatomic molecules in a dilute gas there is a clear separation of time scales:

$$t_c \ll t_f \ll t_{\mathrm{VV}} \ll t_{\mathrm{TV}} \tag{27}$$

We now define a number of parameters which will be useful in estimating the time scales on which various terms are important:

$$\xi_M{}^2 = t_f{}^M/t_{\mathrm{VV}}; \qquad \xi_A{}^2 = t_f{}^A/t_{\mathrm{TV}} \tag{28}$$

$$\lambda_M{}^2 = \xi_M{}^2 t_c/t_f{}^M = t_c/t_{vv}; \qquad \lambda_A{}^2 = \xi_A{}^2 t_c/t_f{}^A = t_c/t_{\mathrm{TV}} \tag{29}$$

where $t_f{}^M$ is the mean free time between molecule–molecule collisions, and $t_f{}^A$ is the mean free time between molecule–atom collisions. The parameters $\lambda_M{}^2$ and $\lambda_A{}^2$ are directly proportional to $1/t_f{}^M$ and $1/t_f{}^A$, respectively. Therefore they go to zero in the limit of low density for any finite values of $\xi_M{}^2$ and $\xi_A{}^2$.

The order of magnitude of the various terms can be estimated by the procedures used in Ref. 8. The order of the master term is

$$(\partial f^n/\partial t)^M = O(\lambda_M{}^2 + \lambda_A{}^2) \tag{30}$$

The order of magnitude of the remainder term is

$$(\partial f^n/dt)^R = O([\lambda_M{}^2 + \lambda_M\lambda_A + \lambda_A{}^2]t_0/t_f) \tag{31}$$

where t_f is the mean free time between any collisions and t_0 is the time, not necessarily finite, for which the integrals in the remainder term do not change appreciably for $t > t_0$. The remainder term can be neglected compared to the master term if $t_0 \ll t_f$.

An analysis similar to that used in Ref. 8 shows that t_0 can be identified with αt_c, where $t_c \ll \alpha t_c \ll t_f$, if, before a collision between particles j and $n + 1$ which leads to a vibrational transition, we have

$$D^{n-1}\mathscr{T}^{n-1}F_M^{n+1} = g_j g_{n+1}\phi_{j,n+1}^2 \mathscr{J}_J^{2}{}_2 D_{j,n+1}^2 D^{n-1}\rho_{\mathrm{vib}}^{n+1} + O(t_c/t_f) \tag{32}$$

This is the condition when particle $n + 1$ is a molecule; the changes necessary when particle $n + 1$ is an atom are obvious.

There are three sufficient conditions for Eq. (32) to hold:

1. The nonvibrational degrees of freedom must be at absolute equilibrium except for terms of $O(t_c/t_f)$.
2. Any time-dependent correlations among the degrees of freedom of a single molecule must be $O(t_c/t_f)$.
3. The vibrational density matrix $\rho_{\mathrm{vib}}^{n+1}$ is energetically diagonal for the molecule or molecules involved in the collision.

The third condition will hold if $\omega_{v^2\bar{v}^2} t_f \gg 1$ for all v^2 and $\bar{v}^2$ for which $\omega_{v^2\bar{v}^2} \neq 0$. This will be true for the molecules under consideration (diatomics with large vibrational spacings) if anharmonicities are ignored.

The first two conditions require that the initial perturbation be small and that

$$t_{\mathrm{VV}} \gg t_{\mathrm{rot}} \gtrsim t_f \tag{33}$$

Vibrational exchange is usually much more efficient that vibration–momentum exchange. In some systems containing only molecules, V–V transitions may be too frequent to allow the translational and rotational degrees of freedom to equilibrate. If there are atoms in the system as well, it will usually be possible to adjust the densities so that V–V transitions will be separated by many collisions and condition (38) holds.

Under the same conditions given above, the initial value term will be of order of magnitude

$$\left(\frac{\partial f^n}{\partial t}\right)^I = O\left(\left[\frac{\lambda_M{}^2}{\xi_M} + \frac{\lambda_A{}^2}{\xi_A}\right]\frac{t_c}{t_f}\right) \tag{34}$$

5. THE MASTER EQUATION

We have shown in Section 4 that under certain conditions the remainder term and the initial value term are of higher order in the density than the master term and can be neglected. Then

$$\partial f^n/\partial t = (\partial f^n/\partial t)^M \tag{35}$$

The master term, Eq. (22), can be rewritten as an equation for the vibrationally diagonal part of the vibrational density matrix:

$$\begin{aligned}\frac{\partial D^n \rho^n_{\mathrm{vib}}}{\partial t} = & -i \lim_{T\to\infty} \frac{N_M}{V} \sum_{j=1}^{n} D_j \mathscr{T}_j \mathscr{L}_{M_j M_{n+1}} G^2_{j,n+1}(T) \mu_j \mu_{n+1} D^2_{j,n+1} D^{n-1} \rho^{n+1}_{\mathrm{vib}}(t) \\ & -i \lim_{T\to\infty} \frac{N_A}{V} \sum_{j=1}^{n} D_j \mathscr{T}_j \mathscr{L}_{M_j A_{n+1}} G^2_{j,n+1}(T) \mu_j \mu_{n+1} D_j D^{n-1} \rho^n_{\mathrm{vib}}(t)\end{aligned} \tag{36}$$

where we have taken the weak coupling limit, $t \to \infty$, $\lambda^2 \to 0$, $\lambda^2 t$ finite, $\lambda = \lambda_M$ or λ_A, and used the fact that

$$-iG^2(s)\theta^2 \exp(iL_0{}^2 s) = (\partial/\partial s)G^2(s) \exp(iL_0{}^2 s) \tag{37}$$

to perform the integrals over s.

We now use a relationship derived by Davis⁽⁵⁾ for the Wigner operators and the results of Andersen and Oppenheim⁽¹²⁾ relating the Liouville formalism to that of the T-matrices of scattering theory to rewrite Eq. (36). We obtain

$$
\begin{aligned}
&\frac{\partial}{\partial t}\langle v^n|\rho^n_{\text{vib}}(t)|\bar{v}^n\rangle\,\Delta(\varepsilon_{v^n},\,\varepsilon_{\bar{v}^n})\\
&\quad = -i\,\frac{N_M}{V}\sum_{v_{n+1}}\sum_{j=1}^{n}\sum_{a^2_{j,n+1}}\Delta(v_j,\,\bar{v}_j)\,\Delta(\varepsilon_{v^{n-1}},\,\varepsilon_{\bar{v}^{n-1}})\\
&\qquad\times\Bigg\{\sum_{\substack{v'^2_{j,n+1}\\ v'_j\neq v_j\\ v'_{n+1}\neq v_{n+1}}}\Delta(\varepsilon_{v'^2},\,\varepsilon_{v^2})[T_{M_jM_{n+1}}(a^2,\,v^2;\,a^2,\,v'^2)\mu^2(a^2,\,v'^2)\\
&\qquad\times\langle v'^2v^{n-1}|\rho^{n+1}_{\text{vib}}(t)|v^2,\,\bar{v}^{n-1}\rangle\\
&\qquad-\mu^2(a^2,\,v^2)\langle v^{n+1}|\rho^{n+1}_{\text{vib}}(t)|v'^2,\,\bar{v}^{n-1}\rangle T^{+}_{M_jM_{n+1}}(a^2,\,v'^2;\,a^2,\,v^2)]\\
&\qquad+2\pi i\sum_{b^2_{j,n+1}}\sum_{\substack{v'^2_{j,n+1}\\ v'_j\neq v''_j\\ v'_{n+1}\neq v''_{n+1}}}\sum_{v''^2_{j,n+1}}\Delta(\varepsilon_{v'^2},\,\varepsilon_{v''^2})T_{M_jM_{n+1}}(a^2,v^2;\,b^2,\,v'^2)\\
&\qquad\times\mu^2(b^2,\,v'^2)\langle v'^2,\,v^{n-1}|\rho^{n+1}_{\text{vib}}(t)|v''^2\bar{v}^{n-1}\rangle T^{+}_{M_jM_{n+1}}(b^2,\,v''^2;\,a^2,\,v^2)\Bigg\}\\
&\qquad+\sum_{v_{n+1}}\sum_{j=1}^{n}\sum_{v'^2_{j,n+1}}\Delta(v_j,\,\bar{v}_j)\,\Delta(\varepsilon_{v^{n-1}},\,\varepsilon_{\bar{v}^{n-1}})\\
&\qquad\times\{B_M(v^2,\,v'^2)\langle v'^2,\,v^{n-1}|\rho^{n+1}_{\text{vib}}(t)|v'^2,\,\bar{v}^{n-1}\rangle\\
&\qquad-B_M(v'^2,\,v^2)\langle v^{n+1}|\rho^{n+1}_{\text{vib}}(t)|v^2,\,\bar{v}^{n-1}\rangle\}\\
&\qquad+\sum_{j=1}^{n}\sum_{v'_j}\Delta(v_j,\,\bar{v}_j)\,\Delta(\varepsilon_{v^{n-1}},\,\varepsilon_{\bar{v}^{n-1}})\{B_A(v_j,\,v_{j'})\\
&\qquad\times\langle v_j',\,v^{n-1}|\rho^{n}_{\text{vib}}(t)|v_j',\,\bar{v}^{n-1}\rangle\\
&\qquad-B_A(v_j',\,v_j)\langle v^n|\rho^{n}_{\text{vib}}(t)|v_j,\bar{v}^{n-1}\rangle\}
\end{aligned}
\tag{38}
$$

where

$$
\begin{aligned}
B_M(v^2_{j,n+1},\,v'^2_{j,n+1}) = \frac{2\pi N_M}{V}\sum_{a^2_{j,n+1}}\sum_{b^2_{j,n+1}}&T_{M_jM_{n+1}}(a^2,\,v^2;\,b^2,\,v'^2)\\
\times\,&T^{+}_{M_jM_{n+1}}(b^2,\,v'^2;\,a^2,\,v^2)\mu^2(b^2,\,v'^2)
\end{aligned}
\tag{39}
$$

$$
\begin{aligned}
B_A(v_j,\,v_j') = \frac{2\pi N_A}{V}\sum_{a^2_{j,n+1}}\sum_{b^2_{j,n+1}}&T_{M_jA_{n+1}}(a^2,\,v_j;\,b^2,\,v_j')\\
\times\,&T^{+}_{M_jA_{n+1}}(b^2,\,v_j';\,a^2,\,v_j)\mu^2(a^2,\,v_j)
\end{aligned}
\tag{40}
$$

Here the T-matrices are assumed to be energetically diagonal and we have applied the optical theorem wherever possible.

This is as simple a form as we can give for the master equation without making important and possibly unjustifiable assumptions about ρ^n_{vib}. For example, if $\rho^n_{\text{vib}}(t)$ is diagonal for all t, the first part of Eq. (38) will vanish, but there is no reason to expect ρ^n_{vib} to be more than energetically diagonal in general. There are two special cases, however. First note that for diatomic molecules $D^1\rho^1_{\text{vib}}(t)$ is diagonal, $D^1\rho^1_{\text{vib}}(t) = P^1(t)$.

Next, if we look at Eq. (38) for $n = 2$, we see that $D^2\rho^2_{\text{vib}}(t)$ must also be diagonal, $D^2\rho^2_{\text{vib}}(t) = P^2(t)$. This implies that Eq. (38) has a particularly simple form for $n = 1$, namely

$$\begin{aligned}(\partial/\partial t)P_{v_1} &= \sum_{v_2}\sum_{v_1'v_2'}[B_M(v^2, v'^2)P^2_{v'^2}(t) - B_M(v'^2, v^2)P^2_{v^2}(t)] \\ &\quad + \sum_{v'_1}[B_A(v_1, v_1')P_{v_1'}(t) - B_A(v_1', v_1)P_{v_1}(t)]\end{aligned} \tag{41}$$

6. INITIALLY UNCORRELATED SYSTEMS

In this section we examine the behavior of our system in the absence of initial correlations. In particular, we will show that if a system has an uncorrelated initial state, then the system will remain uncorrelated for all times.

To show this, assume that the system is initially uncorrelated

$$\langle v^n|\rho^n_{\text{vib}}(0)|v^n\rangle = \prod_{k=1}^{n}\langle v_k|\rho_{\text{vib}}(k, 0)|v_k\rangle = \prod_{k=1}^{n} P_{v_k}(0) \tag{42}$$

Let $P_{v_k}(t)$ be the solution of Eq. (41) with initial state $P_{v_k}(0)$. Then $P^n_{v^n}(t) = \prod^n_{k=1} P_{v_k}(t)$ is a solution of Eq. (38) with initial condition $P^n_{v^n}(0) = \prod^n_{k=1} P_{v_k}(0)$ since from Eqs. (38) and (41) we find that

$$\frac{\partial}{\partial t}P^n_{v^n} = \sum_{j=1}^{n}\prod_{k\neq j}^{n} P_{v_k}\frac{\partial}{\partial t}P_{v_j} = \frac{\partial}{\partial t}\prod_{j=1}^{n} P_{v_j} \tag{43}$$

Therefore if the vibrations are initially uncorrelated, no correlations will ever develop. This result is the same as for systems without interactions among the particles(1) and quite unlike the result found for several systems with interactions.(2,3)

Another consequence is that if there are no vibrational correlations in the system, it will be completely characterized by Eq. (41) and the two-molecule distribution functions on the right-hand side of this equation will factor. The final result is exactly the equation given in Ref. 8 (with the addition of a molecule–atom term).

7. INITIALLY CORRELATED SYSTEMS

In this section we assume that there are initial vibrational correlations and under certain assumptions develop closed equations for the distribution functions $P(t) \equiv P^1(t)$, $P^2(t)$ and the correlation function $U(t)$ defined by

$$U_{12}(t) = P^2_{12}(t) - P_1(t)P_2(t) \tag{44}$$

The correlation function $U(t)$ will be zero if the two particles are uncorrelated, and nonzero if they are correlated.

We have noted before that Eq. (38) is not a closed equation for $\rho^n_{\text{vib}}(t)$ since it contains ρ^{n+1}_{vib}. In order to obtain a closed equation for $P^2(t)$, we use the superposition assumption for $\rho^3_{\text{vib}}(t)$:

$$\rho^3_{\text{vib}}(1, 2, 3, t) = \frac{\rho^2_{\text{vib}}(1, 2, t)\rho^2_{\text{vib}}(1, 3, t)\rho^2_{\text{vib}}(2, 3, t)}{\rho^1_{\text{vib}}(1, \mathrm{t})\rho^1_{\text{vib}}(2, t)\rho^1_{\text{vib}}(3, \mathrm{t})}$$

$$= \frac{P^2_{12}(t)P^2_{13}(t)P^2_{23}(t)}{P_1(t)P_2(t)P_3(t)} \tag{45}$$

Since $\rho^1_{\text{vib}}(t)$ and $\rho^2_{\text{vib}}(t)$ are diagonal, the superposition form for $\rho^3_{\text{vib}}(t)$ is diagonal. The approximation may not be valid if ρ^3_{vib} has important off-diagonal terms.

We will also assume that the system is near equilibrium and linearize our equations. We define a function $p(t)$ by

$$P(t) = {}^0P + p(t) \tag{46}$$

where ${}^0P$ is the equilibrium one-molecule vibrational distribution function. The correlation function $U(t)$ is zero at equilibrium, so the linearized form of $P^2(t)$ in terms of $p(t)$ and $U(t)$ is given by

$$P^2(t) = {}^0P_1{}^0P_2 + {}^0P_1p_2(t) + {}^0P_2p_1(t) + U^2_{12}(t) \tag{47}$$

Furthermore, Eq. (45) can be linearized to give

$$\rho^3_{\text{vib}}(1, 2, 3, t) = {}^0P_1{}^0P_2{}^0P_3 + {}^0P_1U_{23} + {}^0P_2U_{13} + {}^0P_3U_{12} \tag{48}$$

We find an equation for $P(t)$ by recasting Eq. (38) in terms of $p(t)$ and $U(t)$ and linearizing. We obtain

$$\begin{aligned}\frac{d}{dt}P_{v_1} = \sum_{v_2}\sum_{v_1'v_2'} \{&B_M(v^2, v'^2)[{}^0P_{v_1'}{}^0P_{v_2'} + {}^0P_{v_1'}p_{v_2'} + {}^0P_{v_2'}p_{v_1'} + U_{v_1'v_2'}] \\ &- B_M(v'^2, v^2)[{}^0P_{v_1}{}^0P_{v_2} + {}^0P_{v_1}p_{v_2} + {}^0P_{v_2}p_{v_1} + U_{v_1v_2}]\} \\ &+ \sum_{v_1'}\{B_A(v_1, v_1')[{}^0P_{v_1'} + p_{v_1'}] - B_A(v_1', v_1)[{}^0P_{v_1} + p_{v_1}]\}\end{aligned} \tag{49}$$

Then we use Eqs. (47) and (48) in Eq. (38) for $n = 2$ and obtain a linearized equation for $P^2(t)$ in terms of $U(t)$ and $p(t)$. We use this result and Eq. (49) in the relation

$$\frac{dU_{12}}{dt} = \frac{dP^2_{12}}{dt} - P_1\frac{dP_2}{dt} - P_2\frac{dP_2}{dt} \tag{50}$$

and obtain a linear equation for $U(t)$:

$$
\begin{aligned}
\frac{d}{dt} U_{v_1 v_2} = \sum_{v_3} \sum_{v_1' v_3'} & \{B_M(v_{13}^2, v_{13}'^2)[P_{v_1'} U_{v_2 v_3'} + P_{v_3'} U_{v_1' v_2}] \\
& - B_M(v_{13}'^2, v_{13}^2)[P_{v_1} U_{v_2 v_3} + P_{v_3} U_{v_1 v_2}]\} \\
& + \sum_{v_3} \sum_{v_2', v_3'} \{B_M(v_{23}^2, v_{23}'^2)[P_{v_2'} U_{v_1 v_3'} + P_{v_3'} U_{v_1 v_2'}] \\
& - B_M(v_{23}'^2, v_{23}^2)[P_{v_2} U_{v_1 v_3} + P_{v_3} U_{v_1 v_2}]\} \\
& + \sum_{v_1'} \{B_A(v_1, v_1') U_{v_1' v_2} - B_A(v_1', v_2) U_{v_1 v_2}\} \\
& + \sum_{v_2'} \{B_A(v_1, v_2') U_{v_1 v_2'} - B_A(v_2', v_2) U_{v_1 v_2}\}
\end{aligned} \tag{51}
$$

We now have, in Eqs. (49) and (51), a complete set of equations for $U(t)$ and $p(t)$.

8. HARMONIC OSCILLATORS

So far we have made no assumptions about the transition probabilities B_M and B_A. We will now assume that the molecules are harmonic oscillators and use the Landau–Teller approximation for the transition probabilities(13):

$$
\begin{aligned}
B_M(v_{12}^2, \bar{v}_{12}^2) = {} & B_1\{v_1(v_2 + 1)\, \Delta(\bar{v}_1, v_1 - 1)\, \Delta(\bar{v}_2, v_2 + 1) \\
& + (v_1 + 1) v_2\, \Delta(\bar{v}_1, v_1 + 1)\, \Delta(\bar{v}_2, v_2 - 1)\} \\
& + B_2\{v_1 \gamma\, \Delta(\bar{v}_1, v_1 - 1)\, \Delta(\bar{v}_2, v_2) \\
& + (v_1 + 1)\, \Delta(\bar{v}_1, v_1 + 1)\, \Delta(\bar{v}_2, v_2) \\
& + v_2 \gamma\, \Delta(\bar{v}_2, v_2 - 1)\, \Delta(\bar{v}_1, v_1) \\
& + (v_2 + 1)\, \Delta(\bar{v}_2, v_2 + 1)\, \Delta(\bar{v}_1, v_1)\}
\end{aligned} \tag{52}
$$

and

$$
B_A(v_1, \bar{v}_1) = B_3\{v_1 \gamma\, \Delta(\bar{v}_1, v_1 - 1) + (v_1 + 1)\, \Delta|\bar{v}_1, v_1 + 1)\} \tag{53}
$$

where $\gamma = \exp(-\beta\hbar\omega_0)$, $\omega_0 = (\varepsilon_1 - \varepsilon_0)/\hbar$, the vibrational frequency, and the constants B_1, B_2, and B_3 are defined by

$$
\begin{aligned}
B_1 &= B_M(10, 01) = B_M(01, 10) \\
B_2 &= B_M(00, 10) = B_M(00, 01) \\
B_3 &= B_A(0, 1)
\end{aligned} \tag{54}
$$

Note that by the definitions in Eqs. (39) and (40), B_1, B_2, and B_3 contain a density factor, N_M/V or N_A/V.

For a harmonic oscillator the energy levels are $\varepsilon_v = \hbar\omega_0 v$. Hence the equilibrium distribution functions ${}^0P_v$ are

$$
{}^0P_v = [\exp(-\beta\hbar\omega_0 v)] / \sum_v \exp(-\beta\hbar\omega_0 v) = (1 - \gamma)\gamma^v \tag{55}
$$

The functions $p(t)$ and $U(t)$ have the following properties, which follow directly from the definitions and standard properties of distribution functions:

$$\sum_{v} p_v(t) = 0 \tag{56}$$

$$\sum_{v_1} U_{v_1 v_2}(t) = \sum_{v_2} U_{v_1 v_2}(t) = 0 \tag{57}$$

If we now use the Landau–Teller transition probabilities in Eq. (51), use Eqs. (55)–(57), and define the function $Q_v(t)$ by

$$Q_{v_1}(t) = \sum_{v_2} v_2 U_{v_1 v_2}(t) = \sum_{v_2} v_2 U_{v_2 v_1}(t) \tag{58}$$

we can perform the sums over v_3 and obtain

$$\begin{aligned}
\frac{dU_{v_1 v_2}}{dt} \\
= \frac{c}{1-\gamma} \{ & (v_1 + 1) U_{v_1+1, v_2} - [v_1(1+\gamma) + \gamma] U_{v_1 v_2} + \gamma v_1 U_{v_1-1, v_2} \\
& + (v_2 + 1) U_{v_1 v_2 + 1} - [v_2(1+\gamma) + \gamma] U_{v_1 v_2} + \gamma v_2 U_{v_1 v_2 - 1} \} \\
& + (c - a)\{(1-\gamma)^2 [\gamma^{v_1 - 1}(v_1(1-\gamma) - \gamma) Q_{v_2} + \gamma^{v_2 - 1} \\
& \qquad \times (v_2(1-\gamma) - \gamma) Q_{v_1}]\}
\end{aligned} \tag{59}$$

where

$$a = (1 - \gamma)(B_2 + B_3) \tag{60}$$

$$c = B_1 + a = B_1 + (1 - \gamma)(B_2 + B_3) \tag{61}$$

In general we have $c \geqslant a \geqslant 0$. Notice that a depends only on T–V transition rates and will be zero if T–V transitions are not allowed. The constant c depends on both T–V and V–V transition rates.

We do not have a closed equation for $U(t)$ since it depends on $Q_v(t)$. We reduce Eq. (59) to an equation for Q_v by multiplying both sides by v_2, summing over all v_2, and using the fact that

$$\sum_{v} Q_v = \sum_{v_1} \sum_{v_2} v_2 U_{v_1 v_2} = 0 \tag{62}$$

We obtain

$$\begin{aligned}
\frac{dQ_v}{dt} = \frac{c}{1-\gamma} & \{(v+1) Q_{v+1} - [v(1+\gamma) + \gamma] Q_v + \gamma v Q_{v-1}\} - a Q_v \\
& + (c - a)(1-\gamma)^2 \gamma^{v-1} [v(1-\gamma) - \gamma] \, \Delta(t)
\end{aligned} \tag{63}$$

where

$$\Delta(t) = \sum_{v} v Q_v(t) = \sum_{v_1 v_2} v_1 v_2 U_{v_1 v_2}(t) \tag{64}$$

Finally we obtain an equation for $\Delta(t)$ by multiplying both sides of Eq. (63) by v and summing over v:

$$d\Delta(t)/dt = -2a\,\Delta(t) \tag{65}$$

Equations (59), (63), and (65) form a closed set of coupled linear equations for U, Q, and Δ.

Similarly we obtain an equation for $p(t)$ by using the Landau–Teller probabilities in Eq. (49) and performing the sums over v_2. We find

$$\begin{aligned}\frac{dp_v}{dt} = \frac{c}{1-\gamma}\{(v+1)p_{v+1} - [(1+\gamma)v + \gamma]p_v + \gamma v p_{v-1}\}\\ + (c-a)\{(v+1)Q_{v+1} - (2v+1)Q_v + vQ_{v-1}\\ + (1-\gamma)^2\gamma^{v-1}[(1-\gamma)v - \gamma]E(t)\}\end{aligned} \tag{66}$$

where

$$E(t) \equiv \sum_v v p_v = \frac{\overline{\varepsilon(t) - 0_\varepsilon}}{\hbar\omega_0} \tag{67}$$

The new function $E(t)$ is thus proportional to the difference between the average vibrational energy of a molecule at time t and the equilibrium average vibrational energy. An equation for $E(t)$ is obtained by multiplying both sides of Eq. (66) by v and summing over all v:

$$dE(t)/dt = -aE(t) \tag{68}$$

We now have in Eqs. (59), (63), (65), (66), (68), and (47) all the equations needed to find $P(t)$, $P^2(t)$, and $U(t)$.

9. ASYMPTOTIC SOLUTIONS[2] FOR P, P^2, AND U

First we can easily solve Eqs. (65) and (68) for $\Delta(t)$ and $E(t)$:

$$\Delta(t) = \Delta(0)e^{-2at} \tag{69}$$

$$E(t) = E(0)e^{-at} \tag{70}$$

Then we substitute for $\Delta(t)$ in Eq. (63) to obtain

$$\begin{aligned}\frac{dQ_v}{dt} = \frac{c}{1-\gamma}\{(v+1)Q_{v+1} - [v(1+\gamma) + \gamma]Q_{v-1}\} - aQ_v\\ + (c-a)\,\Delta(0)(1-\gamma)^2\gamma^{v-1}[v(1-\gamma) - \gamma]e^{-2at}\end{aligned} \tag{71}$$

We will solve for Q_v by a generating function technique. We define a generating function $\pi(z, t)$ by

$$\pi(z, t) \equiv \sum_v Q_v(t)z^v \tag{72}$$

---

[2] A more detailed version of these calculations is given in Ref. 14.

It satisfies the following equation:

$$\frac{\partial \pi}{\partial t} = \frac{c}{1-\gamma}(1-z)(1-\gamma z)\frac{\partial \pi}{\partial z} - \left[a + \frac{c}{1-\gamma}(1-z)\right]\pi$$
$$- (c-a)\,\Delta(0)(1-\gamma)^2 \frac{1-z}{(1-\gamma z)^2} e^{-2at} \tag{73}$$

The solution of Eq. (73) for initial condition $\pi(z, 0)$ is

$$\pi(z, t) = \frac{(1-\gamma)\pi([1-\gamma z-(1-z)e^{-ct}]/[1-\gamma z-\gamma(1-z)e^{-ct}], 0)}{1-\gamma z-\gamma(1-z)e^{-ct}}$$
$$- \Delta(0)(1-\gamma)^2 \frac{1-z}{1-\gamma z}(e^{-2at} - e^{-at}e^{-ct}) \tag{74}$$

We can find explicit forms for $Q_v(t)$ from Eq. (74) by using the inverse of Eq. (72),

$$Q_v(t) = \frac{1}{v!}\frac{\partial^v}{\partial z^v}\pi(z, t)\bigg|_{z=0} \tag{75}$$

First we expand the first term of Eq. (74), using Eq. (72), and obtain

$$(1-\gamma)e^{-at}\sum_{m=0}^{\infty} Q_m(0)\frac{[1-\gamma z-(1-z)e^{-ct}]^m}{[1-\gamma z-\gamma(1-z)e^{-ct}]^{m+1}} \tag{76}$$

We then expand this in a power series in e^{-ct} and obtain

$$(1-\gamma)e^{-at}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\sum_{k=0}^{\infty} Q_m(0)\binom{m}{k}\binom{n}{k}$$
$$\times (-1)^k(1-\gamma)^k\gamma^{n-k}\frac{(1-z)^n}{(1-\gamma z)^{n+1}}e^{-nct} \tag{77}$$

where $\binom{m}{k}$ and $\binom{n}{k}$ are binomial coefficients. If we now take the appropriate z derivatives, we obtain

$$Q_v(t) = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\binom{m}{k}\binom{n}{k}\binom{n}{l}\binom{v}{l}$$
$$\times Q_m(0)(-1)^{k+l}(1-\gamma)^{k+l+1}\gamma^{n-k+v-l}e^{-nct}e^{-at}$$
$$+ \Delta(0)(1-\gamma)^2\gamma^{v-1}[v(1-\gamma)-\gamma](e^{-2at} - e^{-at}e^{-ct}) \tag{78}$$

We are interested only in the asymptotic behavior of $Q_v(t)$. Since $c \geqslant a$, the only term in the sum over n in Eq. (78) that contributes to the asymptotic solution is $n = 0$. For $n = 0$ we obtain

$$\sum_{m=0}^{\infty} Q_m(0)(1-\gamma)\gamma^v e^{-at} = 0 \tag{79}$$

Therefore the asymptotic solution for $Q_v(t)$ is

$$Q_v(t) \sim \Delta(0)(1-\gamma)^2\gamma^{v-1}[v(1-\gamma)-\gamma]e^{-2at} \tag{80}$$

We now use Eqs. (80) and (70) in Eq. (66) for $p(t)$ to obtain

$$\begin{aligned}\frac{d}{dt}p_v = {} & \frac{c}{1-\gamma}\{(v+1)p_{v+1} - [v(1+\gamma)+\gamma]p_v + \gamma v p_{v-1}\} \\ & + (c-a)\{E(0)(1-\gamma)^2\gamma^{v-1}[v(1-\gamma)-\gamma]e^{-at} \\ & + \Delta(0)(1-\gamma)^3\gamma^{v-2}[(1-\gamma)^2 v(v-1) - 4\gamma(1-\gamma)v + 2\gamma^2]e^{-2at}\}\end{aligned} \tag{81}$$

This equation is solved in exactly the same manner as Eq. (71) for $Q_v(t)$. The result is

$$\begin{aligned}p_v(t) = {} & \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty} P_m(0)\binom{m}{k}\binom{n}{k}\binom{n}{l}\binom{v}{l} \\ & \times (-1)^{k+l}(1-\gamma)^{k+l+1}\gamma^{n-k}\gamma^{v-l}e^{-nct} \\ & + E(0)(1-\gamma)^2\gamma^{v-1}[v(1-\gamma)-\gamma](e^{-at}-e^{ct}) \\ & + \Delta(0)(1-\gamma)^3\gamma^{v-2}[(1-\gamma)v(v-1) - 4\gamma(1-\gamma)v + 2\gamma^2] \\ & \times (e^{-2at}-e^{-2ct})\end{aligned} \tag{82}$$

The asymptotic solution is

$$p_v(t) \sim E(0)(1-\gamma)^2\gamma^{v-1}[v(1-\gamma)-\gamma]e^{-at} \tag{83}$$

We now return to Eq. (59) for $U_{v_1v_2}(t)$ and use the asymptotic solution, Eq. (80), for $Q_v(t)$ to obtain

$$\begin{aligned}\frac{dU_{v_1v_2}}{dt} = {} & \frac{c}{1-\gamma}\{(v_1+1)U_{v_1+1,v_2} - [v_1(1+\gamma)+\gamma]U_{v_1v_2} + \gamma v_1 U_{v_1-1,v_2} \\ & + (v_2+1)U_{v_1v_2+1} - [v_2(1+\gamma)+\gamma]U_{v_1v_2} + \gamma v_2 U_{v_1v_2-1}\} \\ & + (c-a)2\,\Delta(0)(1-\gamma)^4\gamma^{v_1}[v_1(1-\gamma)-\gamma] \\ & \times \gamma^{v_2}[v_2(1-\gamma)-\gamma]e^{-2at}\end{aligned} \tag{84}$$

We define a generating function $\Gamma(y, z, t)$ by

$$\Gamma(y, z, t) = \sum_{v_1v_2} U_{v_1v_2}(t)y^{v_1}z^{v_2} \tag{85}$$

For initial condition $\Gamma(y, z, 0)$ we find the generating function to be

$$\begin{aligned}\Gamma(y, z, t) = {} & \frac{(1-\gamma)^2\Gamma\left(\dfrac{1-\gamma y-(1-y)e^{-ct}}{1-\gamma y-\gamma(1-y)e^{-ct}}, \dfrac{1-\gamma z-(1-z)e^{-ct}}{1-\gamma z-\gamma(1-z)e^{-ct}}, 0\right)}{[1-\gamma y-\gamma(1-y)e^{-ct}][1-\gamma z-\gamma(1-z)e^{-ct}]} \\ & + \Delta(0)(1-\gamma)^4\frac{1-y}{(1-\gamma y)^2}\frac{1-z}{(1-\gamma z)^2}(e^{-2at}-e^{-2ct})\end{aligned}$$

$$
\begin{aligned}
&+ \sum_{n=2}^{\infty} \sum_{m=0}^{\infty} \sum_{k=1}^{n} Q_m(0) \binom{n}{k} \binom{m}{k} (-1)^{k+1} (1-\gamma)^{k+3} \gamma^{n-k} \\
&\times \left[\frac{1-y}{(1-\gamma y)^2} \frac{(1-z)^n}{(1-\gamma z)^{n+1}} + \frac{(1-y)^n}{(1-\gamma z)^{n+1}} \frac{1-z}{(1-\gamma z)^2} \right] \\
&\times (e^{-at} - e^{-ct}) e^{-nct} \qquad (86)
\end{aligned}
$$

We obtain $U_{v_1 v_2}(t)$ explicitly by using the relation

$$
U_{v_1 v_2}(t) = \frac{1}{v_1\,!} \frac{\partial^{v_1}}{\partial y^{v_2}} \frac{1}{v_2\,!} \frac{\partial^{v_2}}{\partial z^{v_2}} \Gamma(y, z, t) \bigg|_{y=0, z=0} \qquad (87)
$$

with the result

$$
\begin{aligned}
U_{v_1 v_2}(t) = &\sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \sum_{k_1=0}^{n_1} \sum_{k_2=0}^{n_2} \sum_{l_1=0}^{n1} \sum_{l_2=0}^{n2} \\
&\times U_{m_1 m_2}(0) \binom{m_1}{k_1} \binom{m_2}{k_2} \binom{n_1}{k_1} \binom{n_2}{k_2} \binom{n_1}{l_1} \binom{n_2}{l_2} \binom{v_1}{l_1} \binom{v_2}{l_2} \\
&\times (-1)^{k_1 + l_1 + k_2 + l_2} (1-\gamma)^{k_1 + l_1 + k_2 + l_2 + 2} \\
&\times \gamma^{n_1 - k_1} \gamma^{n_2 - k_2} \gamma^{v_1 - l_1} \gamma^{v_2 - l_2} e^{-(n_1 + n_2)ct} \\
&+ \Delta(0)(1-\gamma)^2 \gamma^{v_1} [v_1(1-\gamma] \gamma^{v_2} [v_2(1-\gamma) - \gamma] (e^{-2at} - e^{-2ct}) \qquad (88)
\end{aligned}
$$

The sums over n_1 and n_2 in Eq. (88) will be zero unless $n_1 \geqslant 1$ and $n_2 \geqslant 1$; therefore the first term is of order e^{-2ct}. The asymptotic solution for $U(t)$ is thus

$$
\begin{aligned}
U_{v_1 v_2}(t) &\sim \Delta(0)(1-\gamma)^2 \gamma^{v_1} [v_1(1-\gamma) - \gamma] \gamma^{v_2} [v_2(1-\gamma) - \gamma] e^{-2at} \\
&\sim p_{v_1}(t) p_{v_2}(t) \qquad (89)
\end{aligned}
$$

Finally we can find the asymptotic behavior of $P^2(t)$ from Eqs. (47), (83), and (89):

$$
\begin{aligned}
P^2_{v_1 v_2}(t) - {}^0P_{v_1} {}^0P_{v_2} &\sim {}^0P_{v_1} p_{v_2}(t) + {}^0P_{v_2} p_{v_1}(t) \\
&\sim E(0)(1-\gamma)^3 \{\gamma^{v_1 - 1} [v_1(1-\gamma) - \gamma] \\
&\quad + \gamma^{v_2 - 1} [v_2(1-\gamma) - \gamma)\} e^{-at} \qquad (90)
\end{aligned}
$$

Therefore we have shown that the correlation function $U(t)$ decays at a faster rate asymptotically than the distribution functions $P(t)$ and $P^2(t)$.

10. CONCLUSIONS

In the last section we showed that for harmonic oscillators the distribution functions and correlation function decay asymptotically as follows:

$$
\begin{aligned}
P^2(t) - {}^0P_1 {}^0P_2 \to 0 &\quad \text{as} \quad [P(t) - {}^0P] \sim e^{-at} \\
U(t) \to 0 &\quad \text{as} \quad [P(t) - {}^0P]^2 \sim e^{-2at} \qquad (91)
\end{aligned}
$$

This agrees with the results obtained by Oppenheim *et al.*$^{(1,2)}$ for other systems.

We have made many assumptions in deriving Eq. (91). Among other things, we have assumed that the master equation (38) is valid for the system. One important condition is that

$$t_{\mathrm{VV}} \gg t_{\mathrm{rot}} \gtrsim t_{\mathrm{trans}} \tag{92}$$

We can increase t_{VV} relative to t_{rot} by decreasing $\rho_M/\rho_A = N_M/N_A$, the ratio of the density of molecules to that of atoms. For any system at a given temperature and pressure there is a maximum value of ρ_M/ρ_A above which the master equation will no longer be valid.

If the molecules are infinitely dilute in atoms, this corresponds to the special case of $c = a = (1 - \gamma)B_3$, where B_3 is the transition rate for T–V transitions in a molecule–atom collision. The asymptotic solutions Eq. (91) do not change in form since they depend only on a, not on c.

The other special case of interest occurs when $a = 0$, in which case only V–V transitions are allowed. This might occur, for example, at very low temperatures. The distribution functions and the correlation function do not relax to absolute equilibrium (vibrational temperature equal to translational temperature) if $a = 0$. For harmonic oscillator with only V–V transitions, the average vibrational energy of the molecules cannot change. This is reflected in Eq. (70), where $E(t) = E(0)$ for $a = 0$. The more surprising result is that $\Delta(t) = \Delta(0)$ for $a = 0$ and the system will remain correlated for all times if $\Delta(0) \neq 0$. This is a consequence of our assumption that the molecules are harmonic oscillators.$^{(14)}$

Our basic equations for vibrational relaxation are given in Section 5. In Eq. (38) we have a hierarchy of equations similar to the BBGKY hierarchy. For the BBGKY hierarchy, Bogoliubov proposed that after an initial short time the n-particle distribution functions become time-independent functionals of the one-particle distribution functions.$^{(6)}$

We now investigate the validity of this hypothesis in vibrational relaxation. First we note that from the definitions

$$\begin{aligned} P_{12}^2(t) &= U_{12}(t) + P_1(t)P_2(t) \\ &= U_{12}(t) + {}^0P_1{}^0P_2 + {}^0P_1p_2(t) + {}^0P_2p_1(t) + p_1(t)p_2(t) \end{aligned} \tag{93}$$

From Eqs. (83) and (91), we see that

$$P_{12}^2(t) \sim {}^0P_1{}^0P_2 + {}^0P_1p_2(t) + {}^0P_2p_1(t) \tag{94}$$

If asymptotically we use Eq. (94) in Eq. (41) we obtain a closed, asymptotic equation for $P(t)$

$$\begin{aligned} dP_{v_1}/dt = \sum_{v_2}\sum_{v_{12}'^2} \{&B_M(v^2, v'^2)[{}^0P_{v_1'}p_{v_2'} + {}^0P_{v_2'}p_{v_1'}] \\ &- B_M(v'^2, v^2)[{}^0P_{v_1}p_{v_2} + {}^0P_{v_2}p_{v_1}]\} \\ &+ \sum_{v_1'} \{B_A(v_1, v_1')P_{v_1'} - B_A(v_1', v_1)P_{v_1}\} \end{aligned} \tag{95}$$

This, with the addition of a molecule–atom term, is the linearized version of the vibrational master equation given in Ref. 8.

Equations (94) and (95) show that Bogoliubov's hypothesis is true for vibrational relaxation, but the time scales involved are much longer than he had proposed. Since the relaxation time for the vibrational correlations is $1/2a$ while the relaxation time for the system is $1/a$, there is no clear separation of time scales. This occurs, again, because we have focused our attention on quantities which do not depend on center-of-mass positions. The equations that we have derived contain a description of vibrational relaxation only and there is essentially only one time scale $(1/a)$ involved.

REFERENCES

1. I. Oppenheim, K. E. Shuler, and G. H. Weiss, *J. Chem. Phys.* **46**:4100 (1967).
2. I. Oppenheim, K. E. Shuler, and G. H. Weiss, *J. Chem. Phys.* **50**:3662 (1969).
3. D. Bedeaux, K. E. Shuler, and G. H. Weiss, *J. Stat. Phys.* **2**:1 (1970).
4. J. I. Scott and J. M. Deutch, *J. Stat. Phys.* **5**:145 (1972).
5. P. K. Davis, Ph.D. Thesis, Massachusetts Institute of Technology (1970).
6. N. N. Bogoliubov, in *Studies in Statistical Mechanics* (North-Holland, Amsterdam) (1962), Vol. 1.
7. M. S. Green and R. A. Piccirelli, *Phys. Rev.* **132**:1388 (1963).
8. P. K. Davis and I. Oppenheim, *J. Chem. Phys.* **56**:82 (1972).
9. R. Zwanzig, in *Lectures in Theoretical Physics*, Interscience, New York (1961).
10. P. Mazur and J. Biel, *Physica* **32**:1633 (1966).
11. H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics*, North-Holland, Amsterdam (1962), Vol. 1.
12. H. C. Andersen and I. Oppenheim, *Ann. of Phys.* **48**:1 (1968); **57**:1 (1970).
13. L. D. Landau and E. Teller, *Z. Sowjetunion* **10**:321 (1936).
14. J. I. Scott, Ph.D. Thesis, Massachusetts Institute of Technology, (1973).