Approach to Equilibrium in Quantal Systems: Magnetic Resonance*

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The present paper presents a derivation of the "master" or Boltzmann "gain-loss" equation from the Schrödinger equation, i.e., a derivation of the equation for the evolution in time of the probabilities of finding a physical system in its various states from the equation for the corresponding probability amplitudes. The "master" equation is derived for an, in effect completely self-enclosed, "supersystem," [$A+B$], consisting of a "system of interest," [A], and a "surroundings," [B], in relatively weak mutual interaction. A discussion is given of the range of validity of the "master" equation for [$A+B$] and it is shown that the random phase assumption is required for the state vector of [$A+B$] at the initial time only. The normally microcanonical character of the equilibrium statistical configuration of [$A+B$] is demonstrated and a treatment is given of exceptional, "extremely quantal-coherent," initial statistical distributions of [$A+B$] which may evolve away from equilibrium. Derivations are also presented of the "master" equation for [A] and of the "master" equation for an individual particle or quasi-particle [q], within [A]; a discussion of the range of validity of these "master" equations is given and the normally canonical character of the equilibrium statistical configuration of [A] is deduced. General solutions of the "master" equations for [$A+B$], [A], and [q] are worked out and the relation between the principles of "microscopic reversibility" and "detailed balance" and the nonoscillatory character of the approach to equilibrium are exhibited. A theorem is presented regarding the time variation of the entropy of [A].

As illustrations of the general methods developed two important processes in magnetic resonance—the time variation of the longitudinal magnetization, $\langle\mu\rangle_t$, and the time variation of the transverse magnetization, $\langle\mu'\rangle_t$—are discussed in some detail. It is shown that the variation of $\langle\mu\rangle_t$ with t and of $\langle\mu'\rangle_t$ with t for a "nonrigid" lattice can be described by means of the "master" equation for an individual spin [q] and several special cases are discussed on the basis of the evaluation of the appropriate transition probabilities; a comparison with the "spin-temperature" procedure is also appended. On the other hand, it is demonstrated that for a "rigid" lattice no description of the variation of $\langle\mu'\rangle_t$ with t can be given on the basis of a "master" equation; in this case, quantal coherence effects neglected in the derivation of the "master" equation from the Schrödinger equation are vital and $\langle\mu'\rangle_t$ must be evaluated by a rigorous calculation of Trace {[appropriate time dependent density matrix] μ'}.

A. INTRODUCTION

ONE of the major problems in quantum statistical mechanics entails the derivation of the "master" or Boltzmann "gain-loss" equation from the Schrödinger equation, i.e., the derivation of the equation for the evolution in time of the probabilities of finding a physical system in its various states from the equation for the corresponding probability amplitudes. The attack on this problem was initiated by Pauli[1] and recently very important progress has been effected by Van Hove.[2] The discussion below presents a derivation of the "master" equation from the Schrödinger equation using elementary methods and applies the general theory to several magnetic resonance situations.

In brief outline, the subjects treated in the present paper are:

(1) The "master" equation for the "supersystem": derivation from the Schrödinger equation and discussion of range of validity—random phase assumption required for the state vector at the initial time only; deduction of the microcanonical character of the equilibrium statistical configuration of the supersystem; average values of "diagonal" and "nondiagonal" dynamical variables; quantal coherence and possible evolution of the supersystem away from equilibrium.

(2) The "master" equation for the "system of interest": derivation from the "master" equation for the supersystem and discussion of range of validity; deduction of the canonical character of the equilibrium statistical configuration of the system of interest; detailed balance and microscopic reversibility; time variation of the entropy of the system of interest.

(3) The "master" equation for an individual particle or quasi-particle of the system of interest: derivation from the "master" equation for the (whole) system of interest and discussion of range of validity.

(4) The solution of the "master" equation for the supersystem, the system of interest, and the individual particle: spectrum of real relaxation times and nonoscillatory approach to equilibrium; comparison with "spin-temperature" procedure.

(5) Magnetic resonance: time variation of longitudinal magnetization; treatment by means of the individual particle "master" equation; evaluation of appropriate transition probabilities and discussion of several special cases.

(6) Magnetic resonance: time variation of transverse magnetization; case of "rigid" lattice: inapplicability of any "master" equation and discussion of crucial importance of quantal coherence effects neglected in the derivation of the "master" equation from the Schrödinger equation; case of the "nonrigid" lattice: treatment by means of the individual particle "master" equation.

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[1] W. Pauli, *Festschrift zum 60 Geburtstag A. Sommerfeld* (S. Hirzel, Leipzig, 1928), p. 30.

[2] L. Van Hove, Physica **25**, 268 (1959); **23**, 441 (1957); **21**, 517 (1955); see also the instructive papers of W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957); **109**, 1892 (1958).

B. THE "MASTER" OR BOLTZMANN "GAIN-LOSS" EQUATION FOR THE SUPERSYSTEM

We contemplate a "system of interest," $[A]$, considered imbedded in another, in general, larger system, $[B]$, called the "surroundings"; the in effect completely self-enclosed combination: system of interest and surroundings, $[A+B]$, will be called the "supersystem." The Hamiltonian of the supersystem $[A+B]$, $\mathcal{H}$, can then be decomposed as:

$$\mathcal{H}=\mathcal{H}_{[A]}{}^{(0)}+\mathcal{H}_{[B]}{}^{(0)}+\mathcal{V}\equiv\mathcal{H}^{(0)}+\mathcal{V}, \tag{1}$$

where $\mathcal{H}_{[A]}{}^{(0)}$, $\mathcal{H}_{[B]}{}^{(0)}$ are, respectively, the Hamiltonians of $[A]$ when isolated, and of $[B]$ when isolated, and where $\mathcal{V}$ is the interaction Hamiltonian between $[A]$ and $[B]$. In circumstances where $[A]$ and $[B]$ are both macroscopically large, the ratio of $\mathcal{V}$ to $\mathcal{H}^{(0)}$ is $\approx N_{[A]}{}^{\frac{2}{3}}/(N_{[A]}+N_{[B]})\ll 1$ (here $N_{[A]}$, $N_{[B]}$ are the number of atoms in $[A]$, $[B]$, respectively) so that $\mathcal{V}$ can be treated as a relatively small perturbation.

We now choose the complete set of $\mathcal{H}^{(0)}$ eigenstates ψ_n, $\mathcal{H}^{(0)}\psi_n=E_n{}^{(0)}\psi_n$; $E_n{}^{(0)}$ effectively continuous—as basic states for the description of the density matrix operator of $[A+B]$, $\rho(t)$. The matrix elements of $\rho(t)$, $\langle\psi_n|\rho(t)|\psi_m\rangle\equiv\langle n|\rho(t)|m\rangle$, are given by

$$\begin{aligned}\langle n|\rho(t)|m\rangle&\equiv\textstyle\sum_j\langle\psi_n|\psi^{(j)}(t)\rangle\langle\psi^{(j)}(t)|\psi_m|\rangle p_j\\
&=\textstyle\sum_j\langle\psi_n|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\psi^{(j)}(t_0)\rangle\\
&\quad\times\langle\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\psi^{(j)}(t_0)|\psi_m\rangle p_j\\
&=\langle\psi_n|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\textstyle\sum_j\psi^{(j)}(t_0)\rangle\\
&\quad\times\langle\psi^{(j)}(t_0)p_j\exp[(i/\hbar)(t-t_0)\mathcal{H}]|\psi_m\rangle\\
&=\langle n|\{\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\rho(t_0)\\
&\qquad\times\exp[(i/\hbar)(t-t_0)\mathcal{H}]\}|m\rangle;\end{aligned}\tag{2}$$

$$\rho(t)=\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\rho(t_0)\exp[(i/\hbar)(t-t_0)\mathcal{H}]$$

in a physical situation where at the initial time t_0 there is an (incoherent) probability p_j that $[A+B]$ is found in the state $\psi^{(j)}(t_0)$ and where the state $\psi^{(j)}(t_0)$ evolves in time according to the Schrödinger equation:

$$\begin{aligned}\psi^{(j)}(t)&=\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\psi^{(j)}(t_0)\\
&=\exp[-(i/\hbar)(t-t_0)(\mathcal{H}^{(0)}+\mathcal{V})]\psi^{(j)}(t_0);\\
&\qquad t-t_0\geqq 0.\end{aligned}\tag{3}$$

Equations (2), (3) yields for $P(n;t)$, the probability that $[A+B]$ is found at time t in the state ψ_n,[3]

$$\begin{aligned}P(n;t)&=\textstyle\sum_j|\langle\psi_n|\psi^{(j)}(t)\rangle|^2p_j=\langle n|\rho(t)|n\rangle\\
&=\langle n|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\rho(t_0)\\
&\qquad\times\exp[(i/\hbar)(t-t_0)\mathcal{H}]|n\rangle;\end{aligned}\tag{4}$$

$$\textstyle\sum_n P(n;t)=\sum_j p_j=1=\mathrm{Trace}\,\{\rho(t)\},$$

the totality of the $P(n;t)$ values describing the statistical configuration of $[A+B]$ at time t. The average value at time t, $\langle\mathfrak{D}\rangle_t$, of any dynamical variable $\mathfrak{D}$ associated with $[A+B]$ is then:

$$\begin{aligned}\langle\mathfrak{D}\rangle_t&=\sum_j\langle\psi^{(j)}(t)|\mathfrak{D}|\psi^{(j)}(t)\rangle p_j\\
&=\sum_{j,n,m}\langle\psi^{(j)}(t)|\psi_m\rangle\langle\psi_m|\mathfrak{D}|\psi_n\rangle\langle\psi_n|\psi^{(j)}(t)\rangle p_j\\
&=\sum_{n,m}\langle n|\rho(t)|m\rangle\langle m|\mathfrak{D}|n\rangle=\mathrm{Trace}\{\rho(t)\mathfrak{D}\}\\
&=\sum_n P(n;t)\langle n|\mathfrak{D}|n\rangle+\sum_{n,m}(1-\delta_{mn})\\
&\qquad\times\langle n|\rho(t)|m\rangle\langle m|\mathfrak{D}|n\rangle.\end{aligned}\tag{5}$$

Thus, if the matrix of $\mathfrak{D}$ with respect to the ψ_n is diagonal:

$$\langle m|\mathfrak{D}|n\rangle=\langle n|\mathfrak{D}|n\rangle\delta_{mn},$$

the $P(n;t)=\langle n|\rho(t)|n\rangle$ completely describe the dependence of $\langle\mathfrak{D}\rangle_t$ on t and Eq. (5) becomes:

$$\langle\mathfrak{D}^{\mathrm{diag}}\rangle_t=\textstyle\sum_n P(n;t)\langle n|\mathfrak{D}^{\mathrm{diag}}|n\rangle. \tag{6}$$

In what follows we shall in general study "diagonal" dynamical variables $\mathfrak{D}^{\mathrm{diag}}$ with $\langle m|\mathfrak{D}^{\mathrm{diag}}|n\rangle=\langle n|\mathfrak{D}|n\rangle\delta_{mn}$ and we note that all such $\mathfrak{D}^{\mathrm{diag}}$ will necessarily commute with $\mathcal{H}^{(0)}$.

We now consider further the dependence of $P(n;t)$ on t. We have from Eq. (4), with $\tau\geqq 0$:

$$\begin{aligned}&P(n;t+\tau)\\
&\quad=\langle n|\rho(t+\tau)|n\rangle=\langle n|\exp[-(i/\hbar)(t-t_0+\tau)\mathcal{H}]\rho(t_0)\\
&\qquad\times\exp[(i/\hbar)(t-t_0+\tau)\mathcal{H}]|n\rangle\\
&\quad=\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]\rho(t)\exp[(i/\hbar)\tau\mathcal{H}]|n\rangle\\
&\quad=\textstyle\sum_m\tau W_{nm}(\tau)P(m;t)+\tau Y_n(\tau;t-t_0),\end{aligned}\tag{7}$$

where

$$\begin{aligned}&W_{nm}(\tau)\equiv(1/\tau)|\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|m\rangle|^2;\\
&\sum_n\tau W_{nm}(\tau)=\langle m|\exp[(i/\hbar)\tau\mathcal{H}]\\
&\qquad\times\exp[-(i/\hbar)\tau\mathcal{H}]|m\rangle=1;\end{aligned}\tag{8}$$

$$\begin{aligned}&\sum_m\tau W_{nm}(\tau)=\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]\\
&\qquad\times\exp[(i/\hbar)\tau\mathcal{H}]|n\rangle=1,\end{aligned}$$

$$\begin{aligned}Y_n(\tau;t-t_0)&\equiv(1/\tau)\sum_{k,m}(1-\delta_{km})\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|m\rangle\\
&\quad\times\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|k\rangle^*\langle m|\rho(t)|k\rangle\\
&=(1/\tau)\sum_{k,m,l}(1-\delta_{km})\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|m\rangle\\
&\quad\times\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|k\rangle^*\\
&\quad\times\langle m|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|l\rangle\\
&\quad\times\langle k|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|l\rangle^*P(l;t_0)\\
&\quad+(1/\tau)\sum_{k,m,l,q}(1-\delta_{km})(1-\delta_{lq})\\
&\quad\times\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|m\rangle\\
&\quad\times\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|k\rangle^*\\
&\quad\times\langle m|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|l\rangle\\
&\quad\times\langle k|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|q\rangle^*\langle l|\rho(t_0)|q\rangle\\
&=Y_n^*(\tau;t-t_0),\end{aligned}\tag{9}$$

[3] Approximate calculations of $\langle n|\rho(t)|m\rangle$, $\langle n|\rho(t)|n\rangle$ from Eqs. (2)–(4) or the equivalent Eq. (12) below have been given in a magnetic resonance context by R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953); U. Fano, Phys. Rev. **96**, 869 (1954); R. Kubo and K. Tomita, J. Phys. Soc. (Japan) **9**, 888 (1954); F. Bloch, Phys. Rev. **102**, 104 (1956); A. G. Redfield, IBM J. Research Develop. **1**, 19 (1957).

with

$$\exp[-(i/\hbar)\tau\mathcal{H}]=\exp[-(i/\hbar)\tau(\mathcal{H}^{(0)}+\mathcal{V})]$$
$$\equiv\exp[-(i/\hbar)\tau\mathcal{H}^{(0)}](1+\mathcal{S}(\tau)),$$

$$1+\mathcal{S}(\tau)=\exp[(i/\hbar)\tau\mathcal{H}^{(0)}]\exp[-(i/\hbar)\tau(\mathcal{H}^{(0)}+\mathcal{V})]$$
$$=1-(i/\hbar)\mathcal{V}\tau-\tfrac{1}{2}(1/\hbar^2)(\mathcal{V}^2+[\mathcal{V},\mathcal{H}^{(0)}])\tau^2+\cdots$$
$$=1+\sum_{j=1}^{\infty}\left\{(i\hbar)^{-j}\int_0^{\tau}d\tau_1\mathcal{V}(\tau_1)\times\int_0^{\tau_1}d\tau_2\mathcal{V}(\tau_2)\cdots\int_0^{\tau_{j-1}}d\tau_j\mathcal{V}(\tau_j)\right\}$$
$$\equiv 1+\sum_{j=1}^{\infty}\mathcal{S}_j(\tau);\tag{10}$$
$$\mathcal{V}(\tau_q)\equiv\exp[(i/\hbar)\tau_q\mathcal{H}^{(0)}]\mathcal{V}\exp[-(i/\hbar)\tau_q\mathcal{H}^{(0)}].$$

Equations (7) and (8) yield

$$\frac{P(n;t+\tau)-P(n;t)}{\tau}=\sum_m[W_{nm}(\tau)P(m;t)-W_{mn}(\tau)P(n;t)]+Y_n(\tau;t-t_0),\tag{11}$$

which is the basic equation for the subsequent development.

It will be seen that the quantities $W_{nm}(\tau)$ of Eqs. (8), (7), and (11) are (for $n\neq m$) the probabilities per unit time for "transition" of $[A+B]$ during the time interval τ from an "initial" state ψ_m to a "final" state ψ_n under the influence of the interaction $\mathcal{V}$—this follows since any "initial" state ψ_m evolves in time as $\exp[-(i/\hbar)\tau\mathcal{H}]\psi_m$. It should also be noted that, using Eqs. (8) and (9), $\lim_{\tau\to 0}W_{nm}(\tau)=0$ $(n\neq m)$, and

$$\lim_{\tau\to 0}Y_n(\tau;t-t_0)=(i/\hbar)\langle n|[\rho(t),\mathcal{H}]|n\rangle,$$

so that, from Eq. (11),

$$dP(n;t)/dt=(d/dt)\langle n|\rho(t)|n\rangle=\langle n|(i/\hbar)[\rho(t),\mathcal{H}]|n\rangle;\tag{12}$$
$$d\rho(t)/dt=(i/\hbar)[\rho(t),\mathcal{H}]$$

a relation which is usually obtained by direct differentiation with respect to t of Eq. (4) for $P(n;t)=\langle n|\rho(t)|n\rangle$ or of Eq. (2) for $\langle n|\rho(t)|m\rangle$.

We now assume that $\rho(t_0)$ is a "diagonal" dynamical variable

$$\rho(t_0)=\{\rho(t_0)\}^{\text{diag}};$$
$$\langle l|\rho(t_0)|q\rangle=\langle l|\rho(t_0)|l\rangle\delta_{lq}=P(l;t_0)\delta_{lq},\tag{13}$$

so that, substituting into Eq. (9),

$$Y_n(\tau;t-t_0)=(1/\tau)\sum_{k,m,l}(1-\delta_{km})\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|m\rangle\times\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|k\rangle^*\times\langle m|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|l\rangle\times\langle k|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|l\rangle^*P(l;t_0),$$
$$Y_n(\tau;0)=(1/\tau)\sum_{k,m,l}(1-\delta_{km})\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|m\rangle\times\langle n|\exp[-(i/\hbar)\tau\mathcal{H}]|k\rangle^*\delta_{ml}\delta_{kl}P(l;t_0)=0.\tag{14}$$

The assumption $\rho(t_0)=\{\rho(t_0)\}^{\text{diag}}$ implies that the initial statistical distribution of (the ensemble of) $[A+B]$ over the states $\psi^{(j)}(t_0)$ involves no specification of any definite phase relations among the ψ_n; this assumption therefore permits identification of the $\psi^{(j)}(t_0)$, p_j with the ψ_n, $P(n;t_0)$. Thus the assumption $\rho(t_0)=\{\rho(t_0)\}^{\text{diag}}$ implies that quantal interference or coherence effects associated with non-vanishing off-diagonal $\langle l|\rho(t_0)|q\rangle$ are absent in the *initial* time evolution of $[A+B]$ and is equivalent to the so-called random or incoherent phase assumption [1,2] regarding the initial statistical distribution of $[A+B]$ over the ψ_n, i.e., equivalent to the assumption that the state vector of $[A+B]$ at $t=t_0$, $\psi(t_0)$, is given by

$$\psi(t_0)=\sum_n\{[P(n;t_0)]^{\frac{1}{2}}e^{i\beta_n}\}\psi_n$$

with the β_n random. The validity of the assumption $\rho(t_0)=\{\rho(t_0)\}^{\text{diag}}$ is ensured, in most cases of practical interest, by the preparation of the initial physical situation of $[A+B]$ (see Sec. G below for an example).

It is now worth mentioning that $\rho(t_0)=\{\rho(t_0)\}^{\text{diag}}$—Eq. (13)—together with Eqs. (2), (10), yield,

$$\begin{aligned}\langle n|\rho(t)|m\rangle&=\textstyle\sum_k\langle n|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|k\rangle\times\langle m|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|k\rangle^*P(k;t_0)\\&=\exp[-(i/\hbar)(E_n^{(0)}-E_m^{(0)})(t-t_0)]\\&\quad\times\{\delta_{nm}P(m;t_0)+\langle n|\mathcal{S}(t-t_0)|m\rangle P(m;t_0)\\&\quad+\langle m|\mathcal{S}(t-t_0)|n\rangle^*P(n;t_0)\\&\quad+\textstyle\sum_k\langle n|\mathcal{S}(t-t_0)|k\rangle\langle m|\mathcal{S}(t-t_0)|k\rangle^*P(k;t_0)\},\end{aligned}\tag{15}$$

which is, in general, different from zero for $n\neq m$ and $t>t_0$; thus for $t>t_0$, $\rho(t)$ is a "nondiagonal" dynamical variable. For $m=n$, Eq. (15) gives

$$\langle n|\rho(t)|n\rangle=\textstyle\sum_k|\langle n|\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|k\rangle|^2P(k;t_0)$$

which, in view of Eqs. (8) and (4), is equivalent to Eq. (17) below.

We proceed to examine Eq. (11) or Eq. (7), together with Eq. (14), for the dependence of $P(n;t)$ on t; setting $t=t_0$ and writing $t_0+\tau=t'>t_0$, we have,

$$\frac{P(n;t')-P(n;t_0)}{t'-t_0}=\sum_m[W_{nm}(t'-t_0)P(m;t_0)-W_{mn}(t'-t_0)P(n;t_0)],\tag{16}$$

or, using Eq. (8),

$$P(n;t')=\sum_m\{(t'-t_0)W_{nm}(t'-t_0)P(m;t_0)\}. \quad (17)$$

Equation (16) is of the general form of a "master" or Boltzmann "gain-loss" equation for the probability, $P(n;t')$, that $[A+B]$ is found at time t' in the state ψ_n. However the corresponding transition probabilities per unit time, $W_{nm}(t'-t_0)$, are here dependent on $t'-t_0$ and in fact essentially describe the whole actual dependence of $P(n;t')$ on t'—this is best seen from Eq. (17). We should also emphasize that our whole development in Eqs. (2)–(17) [in particular in Eq. (11) and Eq. (16)] is valid with the ψ_n any complete set of states, not necessarily the set of $\mathcal{H}^{(0)}$ eigenstates. The $\mathcal{H}^{(0)}$ eigenstate property of the ψ_n is, however, used to obtain explicit expressions for $W_{nm}(\tau)$ and $Y_n(\tau;t-t_0)$ [see Eqs. (20), (23)–(25), (27)–(34), below].

Equation (16) or Eq. (17) can be conveniently employed to find an explicit form for $P(n;t')$ vs t' for small $t'-t_0$, i.e., for

$$t'-t_0\ll\hbar/|\langle n|\mathcal{V}|m\rangle|\approx\hbar/\xi_n\approx\hbar/\xi_m, \quad (18)$$

where

$$\xi_n\equiv(E_n^{(0)}-E_0^{(0)})/(N_{[A]}+N_{[B]});$$
$$\xi_m\equiv(E_m^{(0)}-E_0^{(0)})/(N_{[A]}+N_{[B]}) \quad (19)$$

are the excitation energies per atom when $[A+B]$ is in the states ψ_n, ψ_m.[4] In fact from Eqs. (8) and (10)

$$\begin{aligned}W_{nm}(t'-t_0)=&\frac{1}{(t'-t_0)}\bigg|\bigg\langle n\bigg|\exp[-(i/\hbar)(t'-t_0)\mathcal{H}^{(0)}]\\&\times\bigg(1-\frac{i\mathcal{V}(t'-t_0)}{\hbar}-\tfrac{1}{2}(\mathcal{V}^2+[\mathcal{V},\mathcal{H}^{(0)}])\\&\times\frac{(t'-t_0)^2}{\hbar^2}+\cdots\bigg)\bigg|m\bigg\rangle\bigg|^2\\=&\frac{1}{(t'-t_0)}\bigg|\delta_{nm}-i\frac{(t'-t_0)}{\hbar}\langle n|\mathcal{V}|m\rangle\\&-\frac{1}{2}\frac{(t'-t_0)^2}{\hbar^2}[\langle n|\mathcal{V}^2|m\rangle\\&+(E_m^{(0)}-E_n^{(0)})\langle n|\mathcal{V}|m\rangle]+\cdots\bigg|^2,\end{aligned} \quad (20)$$

so that, introducing Eq. (20) into Eq. (16)

$$\begin{aligned}P(n;t')=&P(n;t_0)+\sum_m\bigg\{\frac{(t'-t_0)^2}{\hbar^2}|\langle n|\mathcal{V}|m\rangle|^2\\&+\text{terms in }\frac{(t'-t_0)^2}{\hbar^3},\frac{(t'-t_0)^4}{\hbar^4},\cdots\bigg\}\\&\times[P(m;t_0)-P(n;t_0)]\\=&P(n;t_0)\{1-[(t'-t_0)^2/\hbar^2][\langle n|\mathcal{V}^2|n\rangle\\&-(\langle n|\mathcal{V}|n\rangle)^2]+\cdots\}\\&+\sum_m P(m;t_0)\{[(t'-t_0)^2/\hbar^2]\\&\times|\langle n|\mathcal{V}|m\rangle|^2+\cdots\}(1-\delta_{mn}).\end{aligned} \quad (21)$$

The initial relaxation of the $P(n;t')$ from the $P(n;t_0)$ is thus seen to be quadratic in $(t'-t_0)^2$. However the series expansions in Eq. (21) converge rapidly only for $t'-t_0\ll\hbar/|\langle n|\mathcal{V}|m\rangle|\approx\hbar/\xi_n\approx\hbar/\xi_m$ [Eq. (18)] and when $t'-t_0\geqq\hbar/\xi_n$ another method is required to find $P(n;t')$ vs t' from Eqs. (16), (8) or Eqs. (11), (8), and (14).

To describe this other method we consider the Eqs. (11), (8), and (14) under the restrictions:

$$\hbar/\xi_n\ll\tau\leqq t-t_0, \quad (22)$$

$$\begin{aligned}\hbar/\xi_n\ll\tau\ll&[\textstyle\sum_m(2\pi/\hbar)\delta(E_m^{(0)}-E_n^{(0)})\\&\times|\langle m|\mathcal{V}+\mathcal{V}G\mathcal{V}+\cdots|n\rangle|^2(1-\delta_{mn})]^{-1}\\&=[\textstyle\sum_m W_{mn}(\tau)(1-\delta_{mn})]^{-1}\equiv T_n;\end{aligned} \quad (23)$$
$$G\equiv\mathcal{P}[\tfrac{1}{2}(E_m^{(0)}+E_n^{(0)})-\mathcal{H}^{(0)}]^{-1}-i\pi\delta[\tfrac{1}{2}(E_m^{(0)}+E_n^{(0)})-\mathcal{H}^{(0)}];$$

the equality of

$$(2\pi/\hbar)\delta(E_m^{(0)}-E_n^{(0)})|\langle m|\mathcal{V}+\mathcal{V}G\mathcal{V}+\cdots|n\rangle|^2$$

and

$$W_{mn}(\tau)=(1/\tau)|\langle m|\exp[-(i/\hbar)\tau(\mathcal{H}^{(0)}+\mathcal{V})]|n\rangle|^2,$$

for τ subject to the inequalities of Eq. (23) (and $m\neq n$) is a consequence of the application of standard procedures of time dependent perturbation theory[5] to Eqs. (8) and (10) while the quantity T_n is obviously the mean life of $[A+B]$ in the state ψ_n. Equation (23) itself is only possible, of course, if $[A+B]$ is of such a character that

$$\begin{aligned}\hbar/\xi_n\ll&[\textstyle\sum_m(2\pi/\hbar)\delta(E_m^{(0)}-E_n^{(0)})\\&\times|\langle m|\mathcal{V}+\mathcal{V}G\mathcal{V}+\cdots|n\rangle|^2(1-\delta_{mn})]^{-1}\\&=T_n\approx\hbar/\Delta E_n^{(0)},\end{aligned} \quad (24)$$

$$(\Delta E_n^{(0)}\equiv\text{energy width of state }\psi_n),$$

and the inequality of Eq. (24): (excitation energy per particle in state ψ_n)≫(energy width of state ψ_n), is one of the two basic restrictions on the character of $[A+B]$ that must be made to deduce a "master" or Boltzmann

[4] The approximate equality in Eq. (18) of $\langle n|\mathcal{V}|m\rangle$ and ξ_n, ξ_m is a consequence of the fact that

$$\mathcal{V}=\tfrac{1}{2}\textstyle\sum_{i=1}^{N[A]}\sum_{j=1}^{N[B]}v(|\mathbf{R}_i^{[A]}-\mathbf{R}_j^{[B]}|)$$

with a short range $v(|\mathbf{R}_i^{[A]}-\mathbf{R}_j^{[B]}|)$ so that the nonvanishing $|\langle n|\mathcal{V}|m\rangle|$ are $\approx|\langle n|v|m\rangle|\approx|\langle n|v|n\rangle|\approx\xi_n$ or ξ_m, the last approximate equality following from the virial theorem. It is to be noted that $\langle n|v|n\rangle$ will be considerably smaller than ξ_n for Case (II) of Sec. G below [see Eq. (180)].

[5] See, e.g., W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, Oxford, 1954), third edition, Chap. 4. $\mathcal{P}$ in Eq. (23) denotes the Cauchy principal value.

"gain-loss" equation for $P(n;t)$ vs t for $t-t_0 \gg \hbar/\xi_n$ [see (c), (d) after Eq. (35) below].

We now remark that the relation already set down in Eq. (23), viz.,

$$W_{mn}(\tau)=(2\pi/\hbar)\delta(E_m{}^{(0)}-E_n{}^{(0)}) \times |\langle m|\mathcal{V}+\mathcal{V}G\mathcal{V}+\cdots|n\rangle|^2 \quad (25)$$

implies that this $W_{nm}(\tau)$ is actually independent of τ for all τ subject to the inequalities of Eq. (23); we shall also prove below that the $Y_n(\tau;t-t_0)$ of Eq. (14) vanishes up to terms $\approx(\mathcal{V}/\mathcal{H}^{(0)})^3$ if $t-t_0$, τ are subject to the inequalities of Eq. (22). Hence, up to terms $\approx(\mathcal{V}/\mathcal{H}^{(0)})$,[3] the right-hand side of Eq. (11) is effectively independent of τ for all τ, $t-t_0$ satisfying Eqs. (23) and (22) so that the left-hand side of Eq. (11),

$$\frac{P(n;t+\tau)-P(n;t)}{\tau}=\frac{1}{\tau}\int_t^{t+\tau}dt'\frac{dP(n,t')}{dt'}=\frac{dP(n;t)}{dt}+\frac{\tau}{2}\frac{d^2P(n;t)}{dt^2}+\frac{\tau^2}{6}\frac{d^3P(n;t)}{dt^3}+\cdots,$$

must be closely equal to $dP(n;t)/dt$ if it is also to be effectively independent of τ. This last approximation, however, is well justified since for $t-t_0\gg\hbar/\xi_n$ [Eq. (22)] we anticipate that

$$\left|\frac{d^2P(n;t)}{dt^2}\right|\approx\frac{1}{T_n}\left|\frac{dP(n;t)}{dt}\right|;$$
$$\left|\frac{d^3P(n;t)}{dt^3}\right|\approx\frac{1}{T_n}\left|\frac{d^2P(n;t)}{dt}\right|\approx\left(\frac{1}{T_n}\right)^2\left|\frac{dP(n;t)}{dt}\right|,$$

etc. (see Sec. D below) and since $\tau/T_n\ll1$ [Eq. (23)]. Thus Eq. (11) becomes, for $t-t_0\geqq\tau\gg\hbar/\xi_n$, $T_n\gg\tau\gg\hbar/\xi_n$,

$$\frac{dP(n;t)}{dt}=\sum_m[W_{nm}P(m;t)-W_{mn}P(n;t)]+Y_n(\tau;t-t_0);$$
$$W_{nm}\equiv(2\pi/\hbar)\delta(E_n{}^{(0)}-E_m{}^{(0)}) \times|\langle n|\mathcal{V}+\mathcal{V}G\mathcal{V}+\cdots|m\rangle|^2, \quad (26)$$

where it is to be proven that $Y_n(\tau;t-t_0)$ is $\approx(\mathcal{V}/\mathcal{H}^{(0)})^3$ for $t-t_0\geqq\tau\gg\hbar/\xi_n$. Equation (26) shows that the dependence of $P(n;t)$ on t, for $t-t_0\gg\hbar/\xi_n$, and neglecting third and higher powers of $\mathcal{V}/\mathcal{H}^{(0)}$, is governed by a "master" or Boltzmann "gain-loss" equation so that completion of the derivation of this "master" equation from the Eqs. (11), (8), and (14) now only involves the demonstration that $Y_n(\tau;t-t_0)$ is indeed $\approx(\mathcal{V}/\mathcal{H}^{(0)})^3$ for $t-t_0\geqq\tau\gg\hbar/\xi_n$.

We proceed to give this last demonstration and write Eq. (14), using Eq. (10) and with

$$\nu_{km}\equiv(1/\hbar)(E_k{}^{(0)}-E_m{}^{(0)}),$$

in the form:

$$\begin{aligned}
Y_n(\tau;t-t_0)&\\
=(1/\tau)&\sum_{k,m,l}(1-\delta_{km})(\delta_{nm}+\langle n|\mathcal{S}(\tau)|m\rangle)\\
&\times(\delta_{kn}+\langle n|\mathcal{S}(\tau)|k\rangle^*)(\delta_{ml}+\langle m|\mathcal{S}(t-t_0)|l\rangle)\\
&\times(\delta_{lk}+\langle k|\mathcal{S}(t-t_0)|l\rangle^*)e^{i\nu_{km}(t-t_0)}P(l;t_0)\\
=(1/\tau)&\sum_m(1-\delta_{mn})[\langle n|\mathcal{S}(\tau)|m\rangle\langle m|\mathcal{S}(t-t_0)|n\rangle\\
&\times e^{i\nu_{nm}(t-t_0)}P(n;t_0)+\langle n|\mathcal{S}(\tau)|m\rangle\\
&\times\langle m|\mathcal{S}(t-t_0)|n\rangle^*e^{i\nu_{nm}(t-t_0)}P(m;t_0)]+\text{c.c.}\\
&+(1/\tau)\sum_{k,l}\{(1-\delta_{kn})[\langle n|\mathcal{S}(t-t_0)|l\rangle\langle n|\mathcal{S}(\tau)k\rangle^*\\
&\times\langle k|\mathcal{S}(t-t_0)|l\rangle^*e^{i\nu_{kn}(t-t_0)}P(l;t_0)+\text{c.c.}]\\
&+(1-\delta_{kl})[\langle n|\mathcal{S}(\tau)|l\rangle\langle n|\mathcal{S}(\tau)|k\rangle^*\\
&\times\langle k|\mathcal{S}(t-t_0)|l\rangle^*e^{i\nu_{kl}(t-t_0)}P(l;t_0)+\text{c.c.}]\}\\
&+(1/\tau)\sum_{k,m,l}(1-\delta_{km})[\langle n|\mathcal{S}(\tau)|m\rangle\langle n|\mathcal{S}(\tau)|k\rangle^*\\
\times\langle m|\mathcal{S}&(t-t_0)|l\rangle\langle k|\mathcal{S}(t-t_0)|l\rangle^*]e^{i\nu_{km}(t-t_0)}P(l;t_0).
\end{aligned} \quad (27)$$

Further, from Eq. (10)

$$\mathcal{S}_1(\tau)=(i\hbar)^{-1}\int_0^\tau d\tau_1\mathcal{V}(\tau_1)=(i\hbar)^{-1}\int_0^\tau d\tau_1\exp[(i/\hbar)\tau_1\mathcal{H}^{(0)}]\mathcal{V}\times\exp[-(i/\hbar)\tau_1\mathcal{H}^{(0)}]\approx\mathcal{V}; \quad (28)$$

$$\mathcal{S}_2(\tau)=(i\hbar)^{-2}\int_0^\tau d\tau_1\int_0^{\tau_1}d\tau_2\mathcal{V}(\tau_1)\mathcal{V}(\tau_2)\approx\mathcal{V}^2$$

$$\vdots$$

and

$$\langle n|\mathcal{S}_1(\tau)|m\rangle=[(1-e^{i\nu_{nm}\tau})/\hbar\nu_{nm}]\langle n|\mathcal{V}|m\rangle;\quad\cdots$$

so that Eq. (27) becomes, neglecting terms $\approx(\mathcal{V}/\mathcal{H}^{(0)})^3$, $(\mathcal{V}/\mathcal{H}^{(0)})^4$, $\cdots$,

$$Y_n(\tau;t-t_0)=\frac{1}{\tau}\sum_m\left(\frac{1-e^{i\nu_{nm}\tau}}{\hbar\nu_{nm}}\right)\left(\frac{1-e^{i\nu_{nm}(t-t_0)}}{\hbar\nu_{nm}}\right)\times|\langle n|\mathcal{V}|m\rangle|^2[P(n;t_0)-P(m;t_0)]+\text{c.c.}, \quad (29)$$

and it only remains to prove that $Y_n(\tau;t-t_0)$ of Eq. (29) vanishes when $t-t_0$, τ are subject to Eq. (22).

The proof that the $Y_n(\tau;t-t_0)$ of Eq. (29) is actually

zero when $t-t_0$, τ are subject to Eq. (22) can be given as follows. We recall that

$$\sum_m \mathfrak{F}(m) \equiv \sum_{E_m^{(0)},\alpha_m} \mathfrak{F}(E_m^{(0)},\alpha_m) \equiv \int dE_m^{(0)}\eta(E_m^{(0)}) \times \{\mathfrak{F}(E_m^{(0)};\alpha_m)\}_{\text{av over }\alpha_m},$$

where $\eta(E_m^{(0)})$ is the number of $\mathfrak{H}^{(0)}$ eigenstates $\psi_m = \psi_{[A+B]}(E_m^{(0)},\alpha_m)$ with *any* α_m and energy eigenvalues between $E_m^{(0)}$ and $E_m^{(0)}+dE_m^{(0)}$, α_m denoting all quantum numbers other than $E_m^{(0)}$ which characterize the state ψ_m. We can then write Eq. (29) as

$$Y_n(\tau;t-t_0) = \int dE_m^{(0)}\left[f(\xi_m)\left(\frac{1-e^{i\nu_{nm}\tau}}{\hbar\nu_{nm}\tau}\right) \times\left(\frac{1-e^{i\nu_{nm}(t-t_0)}}{\hbar\nu_{nm}}\right)+\text{c.c.}\right], \quad (30)$$

where

$$f(\xi_m) \equiv \eta(E_m^{(0)})\{|\langle E_n^{(0)},\alpha_n|\mathfrak{V}|E_m^{(0)},\alpha_m\rangle|^2 \times[P(E_n^{(0)},\alpha_n;t_0)-P(E_m^{(0)},\alpha_m;t_0)]\}_{\text{av over }\alpha_m} \quad (31)$$

so that, remembering that $\nu_{nm} \equiv (1/\hbar)(E_n^{(0)}-E_m^{(0)}) = (1/\hbar)(\xi_n-\xi_m)(N_{[A]}+N_{[B]})$ [Eq. (19)] and setting $x \equiv \nu_{nm}\tau$, $Y_n(\tau;t-t_0)$ becomes

$$Y_n(\tau;t-t_0) = \hbar^{-1}\int_{-\infty}^{\infty} dx\left[f\left(\xi_n - \frac{x\hbar}{(N_{[A]}+N_{[B]})\tau}\right) \times\left(\frac{1-e^{ix}}{x}\right)\left(\frac{1-e^{i[(t-t_0)/\tau]x}}{x}\right)\right]+\text{c.c.} \quad (32)$$

In Eq. (32), $[(1-e^{ix})/x][(1-e^{i(t-t_0/\tau)x})/x]$ is appreciable numerically only for $|x| \lesssim \pi\tau/(t-t_0) \leqq \pi$. Since now $f(\xi_m)$ is a comparatively slowly varying function of ξ_m, i.e., $\ln f(\xi_m) \approx (N_{[A]}+N_{[B]})(\xi_m/\langle\xi_m\rangle_{\text{av over m}})+\text{const}$, we have

$$f\left(\xi_n - \frac{x\hbar}{(N_{[A]}+N_{[B]})\tau}\right) = f(\xi_n)\left[1+\left(\frac{1}{f(\xi_n)}\right)\left(\frac{df(\xi_n)}{d\xi_n}\right) \times\left(\frac{-x\hbar}{(N_{[A]}+N_{[B]})\tau}\right)+\cdots\right] \approx f(\xi_n)\left[1-\frac{x\hbar/\xi_n}{\tau}+\cdots\right], \quad (33)$$

and this differs from $f(\xi_n)$ by a negligible percent amount since $|x|$ is effectively not larger than $\pi\tau/(t-t_0)$ so that

$$\frac{|x|\hbar/\xi_n}{\tau} \lesssim \frac{\pi\hbar/\xi_n}{\tau}\frac{\tau}{(t-t_0)} \ll 1$$

[Eq. (22)]. Thus Eq. (32) can be written to a very good approximation as

$$Y_n(\tau;t-t_0) = \hbar^{-1}f(\xi_n)\int_{-\infty}^{\infty} dx\left(\frac{1-e^{ix}}{x}\right)\left(\frac{1-e^{i[(t-t_0)/\tau]x}}{x}\right) \equiv \hbar^{-1}f(\xi_n)I\left(\frac{t-t_0}{\tau}\right) \quad (34)$$

and the integral $I([t-t_0]/\tau)$ is zero for all (positive) $(t-t_0)/\tau$ since $[(1-e^{ix})/x][(1-\exp\{i[(t-t_0)/\tau]x\})/x]$ has no poles on the real x axis or in the upper half of the complex x plane and vanishes $\sim 1/|x|^2$ as $|x|\to\infty$.

We have thus deduced from Eq. (11) [or Eq. (26)] the "master" or Boltzmann "gain-loss" equation with time-independent transition probabilities per unit time, W_{nm},

$$\frac{dP(n;t)}{dt} = \sum_m[W_{nm}P(m;t)-W_{mn}P(n;t)];$$
$$W_{nm} \equiv (2\pi/\hbar)\delta(E_n^{(0)}-E_m^{(0)}) \times|\langle n|\mathfrak{V}+\mathfrak{V}G\mathfrak{V}+\cdots|m\rangle|^2, \quad (35)$$

under the restrictions:

(*a*) $\rho(t_0) = \{\rho(t_0)\}^{\text{diag}}$, [Eq. (13)]

(*b*) $\hbar/\xi_n \ll t-t_0$, [Eq. (22)]

(*c*) $\hbar/\xi_n \ll \hbar/\Delta E_n^{(0)} \cong T_n = [\sum_m(2\pi/\hbar) \times\delta(E_m^{(0)}-E_n^{(0)})|\langle m|\mathfrak{V}+\mathfrak{V}G\mathfrak{V}+\cdots|n\rangle|^2 \times(1-\delta_{mn})]^{-1}$, [Eqs. (24), (23)],

(*d*) neglect of terms $\cong(\mathfrak{V}/\mathfrak{H}^{(0)})^3$, $(\mathfrak{V}/\mathfrak{H}^{(0)})^4$, $\cdots$.

in the $Y_n(\tau;t-t_0)$ of Eq. (14) [Eq. (27)–(34)]. It should also be mentioned that with neglect of $\mathfrak{V}G\mathfrak{V}+\cdots$ compared to $\mathfrak{V}$ in the expression for W_{nm} [Eq. (35)] we obtain $W_{nm}=W_{mn}$, i.e., "microscopic reversibility," so that Eq. (35) becomes

$$\frac{dP(n;t)}{dt} = \sum_m W_{nm}[P(m;t)-P(n;t)];$$
$$W_{nm} = (2\pi/\hbar)\delta(E_n^{(0)}-E_m^{(0)})|\langle n|\mathfrak{V}|m\rangle|^2 = (2\pi/\hbar)\delta(E_m^{(0)}-E_n^{(0)})|\langle m|\mathfrak{V}|n\rangle|^2 = W_{mn}. \quad (36)$$

However the validity of "microscopic reversibility," i.e., of the neglect of $\mathfrak{V}G\mathfrak{V}+\cdots$ compared to $\mathfrak{V}$ in the expression for W_{nm}, is not necessary for the derivation of an equation for $dP(n;t)/dt$ of the form of Eq. (36). In fact, in view of the third of the equalities of Eq. (8), we can write Eq. (11) in the form

$$\frac{P(n;t+\tau)-P(n;t)}{\tau} = \sum_m W_{nm}(\tau)[P(m;t)-P(n;t)]+Y_n(\tau;t-t_0), \quad (37)$$

whence, by use of the arguments of Eqs. (22)–(34), we can obtain the analog of Eq. (35):

$$\frac{dP(n;t)}{dt}=\sum_m W_{nm}[P(m;t)-P(n;t)];$$
$$W_{nm}\equiv(2\pi/\hbar)\delta(E_n^{(0)}-E_m^{(0)})\times|\langle n|\mathcal{V}+\mathcal{V}G\mathcal{V}+\cdots|m\rangle|^2, \tag{38}$$

which has the form of Eq. (36).

The solution of Eq. (36) or Eq. (38) is given in Sec. D [Eqs. (75)–(88), (95), (100), (104)–(107)] where it is demonstrated that for $t-t_0\gg T(\max)\equiv$largest of the $T_n\{T_n\equiv[\sum_k W_{kn}(1-\delta_{kn})]^{-1}\}$,

$$\left.\frac{dP(n;t)}{dt}\right]_{t-t_0>>T(\max)}=0, \tag{39}$$

[see especially Eqs. (84), (88), (100)] so that

$$0=\sum_m W_{nm}[P(m;t)|_{t-t_0>>T(\max)}-P(n;t)|_{t-t_0>>T(\max)}]. \tag{40}$$

Equations (39) and (40) show that the various $P(n;t)$ ultimately approach time-persistent values which are quite independent of the corresponding initial values, $P(n;t_0)$.[6] This follows since the quantum numbers $n\equiv E_n^{(0)},\alpha_n;\ m\equiv E_m^{(0)},\alpha_m;\ E_m^{(0)}\cong E_n^{(0)}$, can be chosen so that: $P(n;t)]_{t-t_0>>T(\max)}\leqq P(m;t)]_{t-t_0>>T(\max)}$ for fixed n and all m, whence Eq. (40) implies that actually,

$$P(m;t)|_{t-t_0>>T(\max)}=P(n;t)|_{t-t_0>>T(\max)}=(1/\mathfrak{N})\sum_k P(k;t_0)=1/\mathfrak{N}, \tag{41}$$

where $\mathfrak{N}$ is the number of mutually accessible $\mathcal{H}^{(0)}$ eigenstates of $[A+B]$.[7] Equation (41) states that in the ultimate and time-persistent, i.e., equilibrium, statistical configuration of $[A+B]$ all mutually accessible $\mathcal{H}^{(0)}$ eigenstates are occupied with equal probability.

We now wish to emphasize that the equality of the equilibrium values of the diagonal matrix elements of $\rho(t)$ [Eqs. (41), (4)] by no means implies that $\langle n|\rho(t)|m\rangle|_{t-t_0>>T(\max)}$ vanishes; in fact, such an ultimate vanishing of the off-diagonal matrix elements of $\rho(t)$ would not only contradict the explicit expression for $\langle n|\rho(t)|m\rangle$ given in Eq. (15) [and in Eq. (42) just below] but would also yield

$$\rho(t_0)=\exp[(i/\hbar)(t-t_0)\mathcal{H}]\rho(t)\times\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|_{t-t_0>>T(\max)}$$
$$=\exp[(i/\hbar)(t-t_0)\mathcal{H}]\{(1/\mathfrak{N})1\}\times\exp[-(i/\hbar)(t-t_0)\mathcal{H}]|_{t-t_0>>T(\max)}=(1/\mathfrak{N})1$$

contradicting, in addition, the choice originally made in Eq. (13) for $\rho(t_0)=\{\rho(t_0)\}^{\text{diag}}\neq(1/\mathfrak{N})1$.[8] It should also be mentioned that use of Eqs. (10) and (28) in Eq. (15) for $\langle n|\rho(t)|m\rangle$ yields (for $m\neq n$)

$$\langle n|\rho(t)|m\rangle=\left(\frac{1-e^{-i\nu_{nm}(t-t_0)}}{\hbar\nu_{nm}}\right)\times\langle n|\mathcal{V}|m\rangle(P(n;t_0)-P(m;t_0))+\text{terms}\approx(\mathcal{V}/\mathcal{H}^{(0)})^2,(\mathcal{V}/\mathcal{H}^{(0)})^3,\cdots, \tag{42}$$

which last equation can be employed to estimate those terms in Eq. (5) for $\langle\mathfrak{D}\rangle_t$ which are associated with the off-diagonal matrix elements $\langle m|\mathfrak{D}|n\rangle$ of the now assumed "nondiagonal" dynamical variable, $\mathfrak{D}$. Equations (5) and (42) give, for $t-t_0\gg\hbar/\xi_n,\ \hbar/\xi_m$, and with use of Eqs. (36), (18), (24)

$$\sum_{n,m}(1-\delta_{mn})\langle n|\rho(t)|m\rangle\langle m|\mathfrak{D}|n\rangle$$
$$=\sum_{n,m}(1-\delta_{nm})\left(\frac{1-e^{-i\nu_{nm}(t-t_0)}}{\hbar\nu_{nm}}\right)\langle n|\mathcal{V}|m\rangle\times(P(n;t_0)-P(m;t_0))\langle m|\mathfrak{D}|n\rangle$$
$$\cong i\sum_{n,m}(1-\delta_{mn})[(2\pi/\hbar)\delta(E_n^{(0)}-E_m^{(0)})\times|\langle n|\mathcal{V}|m\rangle|^2](P(n;t_0)-P(m;t_0))\frac{\langle m|\mathfrak{D}|n\rangle}{\langle m|\mathcal{V}|n\rangle}\frac{\hbar}{2}$$
$$\approx\left|\sum_{n,m}(1-\delta_{mn})W_{nm}P(m;t_0)\langle m|\mathfrak{D}|n\rangle(\hbar/\xi_m)\right|$$
$$=\left|\sum_m P(m;t_0)\{\langle m|\mathfrak{D}|n\rangle\}_{\text{av over }n}(\hbar/\xi_m)/T_m\right|$$
$$\approx\left|\{\langle m|\mathfrak{D}|n\rangle\}_{\text{av over }n,m}\right|\{(\hbar/\xi_m)/T_m\}_{\text{av over }m}\ll\left|\{\langle m|\mathfrak{D}|n\rangle\}_{\text{av over }n,m}\right|. \tag{43}$$

Thus, provided that

$$\left|\{\langle n|\mathfrak{D}|n\rangle\}_{\text{av over }n}\right|\gg\left|\{\langle m|\mathfrak{D}|n\rangle\}_{\text{av over }n,m}\right|\times\{(\hbar/\xi_m)/T_m\}_{\text{av over }m}, \tag{44}$$

which, in view of Eq. (24), is certainly satisfied if

$$\left|\{\langle n|\mathfrak{D}|n\rangle\}_{\text{av over }n}\right|\gtrsim\left|\{\langle m|\mathfrak{D}|n\rangle\}_{\text{av over }n,m}\right|, \tag{45}$$

we have from Eqs. (43) and (5)

$$\langle\mathfrak{D}\rangle_t=\langle\mathfrak{D}^{\text{nondiag}}\rangle\cong\sum_n P(n;t)\langle n|\mathfrak{D}^{\text{nondiag}}|n\rangle;\quad t-t_0\gg\hbar/\xi_n, \tag{46}$$

whence, using Eq. (41),

$$\langle\mathfrak{D}\rangle_t=\langle\mathfrak{D}^{\text{nondiag}}\rangle_t\cong(1/\mathfrak{N})\sum_n\langle n|\mathfrak{D}^{\text{nondiag}}|n\rangle;\quad t-t_0\gg T(\max)\gg\hbar/\xi_n, \tag{47}$$

while, from Eqs. (41), (6)

$$\langle\mathfrak{D}\rangle_t=\langle\mathfrak{D}^{\text{diag}}\rangle_t=(1/\mathfrak{N})\sum_n\langle n|\mathfrak{D}^{\text{diag}}|n\rangle;\quad t-t_0\gg T(\max)\gg\hbar/\xi_n. \tag{48}$$

[6] It will also be seen in Sec. D that the $P(n;t)$ approach their ultimate and time-persistent, i.e., equilibrium, values in a nonoscillatory fashion.

[7] Since $W_{nm}\propto\delta(E_n^{(0)}-E_m^{(0)})$ [Eqs. (38) or (36)] all such mutually accessible $\mathcal{H}^{(0)}$ eigenstates have approximately equal eigenvalues: $E_n^{(0)}\cong E_m^{(0)}$.

[8] It should be particularly noted that however $\rho(t_0)$ is taken, e.g., with arbitrary $\langle n|\rho(t_0)|m\rangle$ $(m\neq n)$, $\rho(t)=\exp[-(i/\hbar)\times(t-t_0)\mathcal{H}]\rho(t_0)\exp[(i/\hbar)(t-t_0)\mathcal{H}]$ cannot ever become $(1/\mathfrak{N})1$ except in the special case $\rho(t_0)=(1/\mathfrak{N})1$ when $\rho(t)$ is also $(1/\mathfrak{N})1$ for all $t\geqq t_0$.

Equations (47), (48) indicate that, in the equilibrium statistical configuration of $[A+B]$, average values of "nondiagonal" as well as "diagonal" dynamical variables $\mathfrak{D}$ are obtained by averaging the expectation value of $\mathfrak{D}$ in a particular $\mathcal{H}^{(0)}$ eigenstate, ψ_n, over all mutually accessible ψ_n with the same weight, $1/\mathfrak{N}$, attached to each ψ_n. This mode of averaging is precisely that which would be adopted if a microcanonical ensemble were assigned to $[A+B]$ and our demonstration of Eqs. (47), (48) is therefore equivalent to a justification of the assignment of such a microcanonical ensemble to the supersystem $[A+B]$ in its ultimate and time-persistent equilibrium statistical configuration, i.e., equivalent to a demonstration [under the restrictions (a)–(d) above and the further restrictions (e), (f) below] of the quantal ergodic character of the supersystem.

It remains to discuss the possible effect of the neglect of the terms $\approx(\mathcal{V}/\mathcal{H}^{(0)})^3$, $(\mathcal{V}/\mathcal{H}^{(0)})^4$, $\cdots$, in passing from the $Y_n(\tau;t-t_0)$ of Eq. (27) to the $Y_n(\tau;t-t_0)$ of Eq. (29) [restriction (d) above]. Since $\mathcal{V}/\mathcal{H}^{(0)} \approx N_{[A]}^{\frac{1}{3}}/(N_{[A]}+N_{[B]})$ [see discussion after Eq. (1)] this neglect is better and better justified for larger and larger $[A+B]$; on the other hand, the Poincaré recurrence time, $\mathcal{T}(\delta)$, defined by

$$\frac{|P(n;t_0+\mathcal{T}(\delta))-P(n;t_0)|}{P(n;t_0)} \leqq \delta \tag{49}$$

(for all n; δ, a preassigned arbitrarily small number, say 1/100) approaches infinity as $[A+B]$ grows larger and larger. It is thus reasonable to conjecture that the terms $\approx(\mathcal{V}/\mathcal{H}^{(0)})^3$, $(\mathcal{V}/\mathcal{H}^{(0)})^4$, $\cdots$ in the $Y_n(\tau;t-t_0)$ are associated with the actual quasiperiodicity of the time evolution of $[A+B]$, i.e., are associated with the Poincaré recurrence phenomenon in $[A+B]$, and that our neglect of these terms corresponds, among other things, to the assumption that the $\mathcal{T}(\delta)$ of $[A+B]$ is effectively infinite. If this conjecture is correct another pair of restrictions:

$$(e)\quad (t-t_0)\ll\mathcal{T}(\delta), \qquad\qquad (f)\quad T(\max)\ll\mathcal{T}(\delta),$$

must be added to the list of restrictions (a)–(d), above, required for the validity of the "master" or Boltzmann "gain-loss" Eqs. (35) or (38) or (36); as a consequence Eqs. (41), (47), (48) should, strictly speaking, be written as:

$$P(m;t)\,|_{\mathcal{T}(\delta)>>t-t_0>>T(\max)} = P(n;t)\,|_{\mathcal{T}(\delta)>>t-t_0>>T(\max)} = (1/\mathfrak{N})\textstyle\sum_k P(k;t_0)=1/\mathfrak{N}, \tag{50}$$

$$\langle\mathfrak{D}\rangle_t=\langle\mathfrak{D}^{\text{nondiag}}\rangle_t \cong (1/\mathfrak{N})\textstyle\sum_n\langle n|\,\mathfrak{D}^{\text{nondiag}}|\,n\rangle; \quad \mathcal{T}(\delta)\gg t-t_0\gg T(\max)\gg\hbar/\xi_n, \tag{51}$$

$$\langle\mathfrak{D}\rangle_t=\langle\mathfrak{D}^{\text{diag}}\rangle_t=(1/\mathfrak{N})\textstyle\sum_n\langle n|\,\mathfrak{D}^{\text{diag}}|\,n\rangle; \quad \mathcal{T}(\delta)\gg t-t_0\gg T(\max)\gg\hbar/\xi_n. \tag{52}$$

In concluding this section we wish to emphasize that we have shown, subject to the restrictions (a)–(f), that once the equilibrium statistical configuration is attained it persists in time; thus it is impossible [at least during time intervals $\ll\mathcal{T}(\delta)$] for an equilibrium statistical configuration to evolve into a nonequilibrium statistical configuration. Since in addition, any nonequilibrium statistical configuration evolves in a nonoscillatory way[6] toward the equilibrium statistical configuration, we have demonstrated, again subject to the restrictions (a)–(f), the essential irreversibility of the time evolution of the statistical configuration of $[A+B]$. The reconciliation of this irreversibility with the reversibility of the time evolution of $\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\times\psi^{(j)}(t_0)$ [Eq. (3)] which implies a corresponding reversibility in the time evolution of

$$\rho(t)=\exp[-(i/\hbar)(t-t_0)\mathcal{H}]\rho(t_0)\exp[(i/\hbar)(t-t_0)\mathcal{H}]$$

[Eq. (2)] is effected by the observation that very special, "extremely quantal-coherent," initial statistical distributions, associated at a minimum with a "nondiagonal" $\rho(t_0)$ and thus certainly violating restriction (a), are required to produce processes which can be appropriately described as the evolution of an initial nonequilibrium statistical configuration of $[A+B]$ into statistical configurations of $[A+B]$ still further from equilibrium (see Appendix A).

C. THE "MASTER" OR BOLTZMANN "GAIN-LOSS" EQUATION FOR THE SYSTEM OF INTEREST

To deduce the "master" equation for the system of interest we express the states $\psi_n\equiv\psi_{[A+B]}(E_n^{(0)},\gamma_n)$ of the supersystem $[A+B]$ in terms of the states $\psi_{[A]}(\epsilon_j,\alpha_j)$, $\psi_{[B]}(\eta_u,\beta_u)$ of the system of interest $[A]$ and the surroundings $[B]$, as:

$$\begin{aligned}
&\psi_{[A+B]}(E_n^{(0)},\gamma_n)=\psi_{[A]}(\epsilon_j,\alpha_j)\psi_{[B]}(\eta_u,\beta_u),\\
&\mathcal{H}^{(0)}\psi_{[A+B]}(E_n^{(0)},\gamma_n)\equiv\{\mathcal{H}_{[A]}{}^{(0)}+\mathcal{H}_{[B]}{}^{(0)}\}\psi(E_n^{(0)},\gamma_n)\\
&\quad=\psi_{[B]}(\eta_u,\beta_u)\{\mathcal{H}_{[A]}{}^{(0)}\psi_{[A]}(\epsilon_j,\alpha_j)\}\\
&\qquad\qquad+\psi_{[A]}(\epsilon_j,\alpha_j)\{\mathcal{H}_{[B]}{}^{(0)}\psi_{[B]}(\eta_u,\beta_u)\}\\
&\quad=(\epsilon_j+\eta_u)\psi_{[A]}(\epsilon_j,\alpha_j)\psi_{[B]}(\eta_u,\beta_u)\\
&\quad=E_n^{(0)}\psi_{[A+B]}(E_n^{(0)},\gamma_n),
\end{aligned} \tag{53}$$

where α_j, β_u, $\gamma_n\equiv\alpha_j$ and β_u are quantum numbers other than the energy eigenvalues ϵ_j, η_u, $E_n^{(0)}=\epsilon_j+\eta_u$ characterizing the states $\psi_{[A]}(\epsilon_j;\alpha_j)$, $\psi_{[B]}(\eta_u,\beta_u)$, and $\psi_{[A+B]}(E_n^{(0)},\gamma_n)$. We next consider

$$P(n;t)\equiv P_{[A+B]}(\epsilon_j,\alpha_j;\eta_u,\beta_u;t) \tag{54}$$

as the joint probability that $[A]$, $[B]$ are found in the states $\psi_{[A]}(\epsilon_j,\alpha_j)$, $\psi_{[B]}(\eta_u,\beta_u)$ at time t, equal identically to the probability that $[A+B]$ is found in the state $\psi_{[A+B]}(E_n^{(0)},\gamma_n)$ $[=\psi_{[A]}(\epsilon_j,\alpha_j)\psi_{[B]}(\eta_u,\beta_u)]$ at time t, and define

$$P_{[A]}(\epsilon_j,\alpha_j;t)=\sum_{\eta_u,\beta_u} P_{[A+B]}(\epsilon_j,\alpha_j;\eta_u,\beta_u;t)=\sum_{\beta_u} P_{[A+B]}(\epsilon_j,\alpha_j;E_n^{(0)}-\epsilon_j,\beta_u;t),$$
$$P_{[B]}(\eta_u,\beta_u;t)\equiv\sum_{\epsilon_j,\alpha_j} P_{[A+B]}(\epsilon_j,\alpha_j;\eta_u,\beta_u;t)=\sum_{\alpha_j} P_{[A+B]}(E_n^{(0)}-\eta_u,\alpha_j;\eta_u,\beta_u;t), \tag{55}$$

as, respectively, the probability at time t that $[A]$ is found in the state $\psi_{[A]}(\epsilon_j,\alpha_j)$ for any probability distribution of $[B]$ over the various states $\psi_{[B]}(\eta_u;\beta_u)$ and the probability at time t that $[B]$ is found in the state $\psi_{[B]}(\eta_u,\beta_u)$ for any probability distribution of $[A]$ over the various states $\psi_{[A]}(\epsilon_j;\alpha_j)$. The "master" equation for $P_{[A+B]}(\epsilon_j,\alpha_j;\eta_u,\beta_u;t)$, Eq. (35), together with Eq. (55), then yields, with

$$W_{nm}\equiv W_{[A+B]}(\epsilon_j,\alpha_j,\eta_u,\beta_u;\epsilon_k,\alpha_k,\eta_v,\beta_v),$$
$$W_{mn}\equiv W_{[A+B]}(\epsilon_k,\alpha_k,\eta_v,\beta_v;\epsilon_j,\alpha_j,\eta_u,\beta_u),$$
$$E_n^{(0)}=\epsilon_j+\eta_u\cong\epsilon_k+\eta_v=E_m^{(0)}\equiv E,$$

$$\frac{d}{dt}P_{[A]}(\epsilon_j,\alpha_j;t)=\sum_{\epsilon_k,\alpha_k}[w_{[A]}(\epsilon_j,\alpha_j;\epsilon_k,\alpha_k;t)\times P_{[A]}(\epsilon_k,\alpha_k;t)-w_{[A]}(\epsilon_k,\alpha_k;\epsilon_j,\alpha_j;t)\times P_{[A]}(\epsilon_j,\alpha_j;t)], \tag{56}$$

where

$$w_{[A]}(\epsilon_j,\alpha_j;\epsilon_k,\alpha_k;t)\equiv\frac{\sum_{\beta_u,\beta_v} W_{[A+B]}(\epsilon_j,\alpha_j,E-\epsilon_j,\beta_u;\epsilon_k,\alpha_k,E-\epsilon_k,\beta_v)P_{[A+B]}(\epsilon_k,\alpha_k;E-\epsilon_k,\beta_v;t)}{\sum_{\beta_v} P_{[A+B]}(\epsilon_k,\alpha_k;E-\epsilon_k,\beta_v;t)}$$
$$w_{[A]}(\epsilon_k,\alpha_k;\epsilon_j,\alpha_j;t)\equiv\frac{\sum_{\beta_u,\beta_v} W_{[A+B]}(\epsilon_k,\alpha_k,E-\epsilon_k,\beta_v;\epsilon_j,\alpha_j,E-\epsilon_j,\beta_u)P_{[A+B]}(\epsilon_j,\alpha_j;E-\epsilon_j,\beta_u;t)}{\sum_{\beta_u} P_{[A+B]}(\epsilon_j,\alpha_j;E-\epsilon_j;\beta_u;t)}, \tag{57}$$

and

$$\frac{d}{dt}P_{[B]}(\eta_u,\beta_u;t)=\sum_{\eta_v,\beta_v}[w_{[B]}(\eta_u,\beta_u;\eta_v,\beta_v;t)P_{[B]}(\eta_v,\beta_v;t)-w_{[B]}(\eta_v,\beta_v;\eta_u,\beta_u;t)P_{[B]}(\eta_u,\beta_u;t)], \tag{58}$$

where

$$w_{[B]}(\eta_u,\beta_u;\eta_v,\beta_v;t)\equiv\frac{\sum_{\alpha_j,\alpha_k} W_{[A+B]}(E-\eta_u,\alpha_j;\eta_u,\beta_u;E-\eta_v,\alpha_k,\eta_v,\beta_v)P_{[A+B]}(E-\eta_v,\alpha_k;\eta_v,\beta_v;t)}{\sum_{\alpha_k} P_{[A+B]}(E-\eta_v,\alpha_k;\eta_v,\beta_v;t)}$$
$$w_{[B]}(\eta_v,\beta_v;\eta_u,\beta_u;t)\equiv\frac{\sum_{\alpha_j,\alpha_k} W_{[A+B]}(E-\eta_v,\alpha_k,\eta_v,\beta_v;E-\eta_u,\alpha_j,\eta_u\,\beta_u)P_{[A+B]}(E-\eta_u,\alpha_j;\eta_u,\beta_u;t)}{\sum_{\alpha_j} P_{[A+B]}(E-\eta_u,\alpha_j;\eta_u,\beta_u;t)}. \tag{59}$$

Equations (56)–(59) for $P_{[A]}(\epsilon_j,\alpha_j;t)$, $P_{[B]}(\eta_u,\beta_u;t)$ are of the "master" or Boltzmann "gain-loss" type with, however, time-dependent transition probabilities per unit time:

$$w_{[A]}(\epsilon_j,\alpha_j;\epsilon_k,\alpha_k;t),\ \cdots,\ w_{[B]}(\eta_v,\beta_v;\eta_u,\beta_u;t).$$

We first consider the ultimate and time-persistent equilibrium statistical configuration of $[A+B]$. In this case $\mathcal{T}(\delta)\gg t-t_0\gg T(\max)$ (see Sec. B above) and from Eqs. (41), (50), and (54):

$$P_{[A+B]}(\epsilon_k,\alpha_k;\eta_v,\beta_v;t)=P_{[A+B]}(\epsilon_j,\alpha_j;\eta_u,\beta_u;t)=1/\mathfrak{N}\quad(\epsilon_j+\eta_u\cong\epsilon_k+\eta_v\equiv E),$$

so that, using Eqs. (55), (57), and (59), and with $\mathfrak{N}_{[A]}(\epsilon_j)$, $\mathfrak{N}_{[B]}(\eta_u)$ the numbers of $[A]$, $[B]$ energy eigenstates with energy eigenvalues ϵ_j, η_u,

$$P_{[A]}^{\text{equil}}(\epsilon_j;\alpha_j;t)=\mathfrak{N}_{[B]}(E-\epsilon_j)/\mathfrak{N},$$
$$\sum_{\epsilon_j,\alpha_j} P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)=\sum_{\epsilon_j,\alpha_j}\mathfrak{N}_{[B]}(E-\epsilon_j)/\mathfrak{N}=(1/\mathfrak{N})\sum_{\epsilon_j}\mathfrak{N}_{[A]}(\epsilon_j)\mathfrak{N}_{[B]}(E-\epsilon_j)=1,$$
$$P_{[B]}^{\text{equil}}(\eta_u,\beta_u;t)=\mathfrak{N}_{[A]}(E-\eta_u)/\mathfrak{N}, \tag{60}$$
$$\sum_{\eta_u,\beta_u} P_{[B]}^{\text{equil}}(\eta_u,\beta_u;t)=\sum_{\eta_u,\beta_u}\mathfrak{N}_{[A]}(E-\eta_u)/\mathfrak{N}=(1/\mathfrak{N})\sum_{\eta_u}\mathfrak{N}_{[B]}(\eta_u)\mathfrak{N}_{[A]}(E-\eta_u)=1,$$
$$w_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;\epsilon_k,\alpha_k;t)=\frac{\sum_{\beta_u,\beta_v} W_{[A+B]}(\epsilon_j,\alpha_j,E-\epsilon_j,\beta_u;\epsilon_k,\alpha_k,E-\epsilon_k,\beta_v)}{\mathfrak{N}_{[B]}(E-\epsilon_k)},$$

$$
\begin{aligned}
w_{[A]}{}^{\text{equil}}(\epsilon_k,\alpha_k;\,\epsilon_j,\alpha_j;\,t)&=\frac{\sum_{\beta_u,\beta_v} W_{[A+B]}(\epsilon_k,\,\alpha_k,\,E-\epsilon_k,\,\beta_v;\,\epsilon_j,\,\alpha_j,\,E-\epsilon_j,\,\beta_u)}{\mathfrak{N}_{[B]}(E-\epsilon_j)},\\
w_{[B]}{}^{\text{equil}}(\eta_u,\beta_u;\,\eta_v,\beta_v;\,t)&=\frac{\sum_{\alpha_j,\alpha_k} W_{[A+B]}(E-\eta_u,\,\alpha_j,\,\eta_u,\,\beta_u;\,E-\eta_v,\,\alpha_k,\,\eta_v,\,\beta_v)}{\mathfrak{N}_{[A]}(E-\eta_v)},\\
w_{[B]}{}^{\text{equil}}(\eta_v,\beta_v;\,\eta_u,\beta_u;\,t)&=\frac{\sum_{\alpha_j,\alpha_k} W_{[A+B]}(E-\eta_v,\,\alpha_k,\,\eta_v,\,\beta_v;\,E-\eta_u,\,\alpha_j,\,\eta_u,\,\beta_u)}{\mathfrak{N}_{[A]}(E-\eta_u)}.
\end{aligned}
\tag{61}
$$

Equations (61), (60) and the "microscopic reversibility" of the $W_{[A+B]}$ [Eq. (36)] imply the principle of "detailed balance":

$$
\begin{aligned}
w_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,\epsilon_k,\alpha_k;\,t)P_{[A]}{}^{\text{equil}}(\epsilon_k,\alpha_k;\,t)&=w_{[A]}{}^{\text{equil}}(\epsilon_k,\alpha_k;\,\epsilon_j,\alpha_j;\,t)P_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,t),\\
w_{[B]}{}^{\text{equil}}(\eta_u,\beta_u;\,\eta_v,\beta_v;\,t)P_{[B]}{}^{\text{equil}}(\eta_v,\beta_v;\,t)&=w_{[B]}{}^{\text{equil}}(\eta_v,\beta_v;\,\eta_u,\beta_u;\,t)P_{[B]}{}^{\text{equil}}(\eta_u,\beta_u;\,t)
\end{aligned}
\tag{62}
$$

which result is sufficient for these time-persistent and ultimate $P_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,t)$, $P_{[B]}{}^{\text{equil}}(\eta_u,\beta_u;\,t)$ of Eq. (60) to satisfy identically the "master" Eqs. (56), (58).

We may also write, in view of Eq. (60)

$$
\begin{aligned}
P_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,t)&=\frac{\mathfrak{N}_{[B]}(E-\epsilon_j)}{\sum_{\epsilon_k}\mathfrak{N}_{[A]}(\epsilon_k)\mathfrak{N}_{[B]}(E-\epsilon_k)}=\frac{\mathfrak{N}_{[B]}(E-\epsilon_j)}{\sum_{\epsilon_k,\alpha_k}\mathfrak{N}_{[B]}(E-\epsilon_k)}\cong\frac{e^{-\epsilon_j/\Theta}}{\sum_{\epsilon_k,\alpha_k}e^{-\epsilon_k/\Theta}};\quad \Theta^{-1}\equiv(kT)^{-1}\equiv\frac{d}{dE}\ln\mathfrak{N}_{[B]}(E),\\
P_{[B]}{}^{\text{equil}}(\eta_u,\beta_u;\,t)&=\frac{\mathfrak{N}_{[A]}(E-\eta_u)}{\sum_{\eta_v}\mathfrak{N}_{[B]}(\eta_v)\mathfrak{N}_{[A]}(E-\eta_v)}=\frac{\mathfrak{N}_{[A]}(E-\eta_u)}{\sum_{\eta_v,\beta_v}\mathfrak{N}_{[A]}(E-\eta_v)}\cong\frac{1}{\mathfrak{N}_{[B]}(E)}\frac{\mathfrak{N}_{[A]}(E-\eta_u)}{\sum_{\eta_v}\mathfrak{N}_{[A]}(E-\eta_v)}\cong\frac{1}{\mathfrak{N}_{[B]}(E)},
\end{aligned}
\tag{63}
$$

provided that the system of interest $[A]$ is so much smaller than the surroundings $[B]$ ($N_{[A]}\ll N_{[B]}$) that the various states $\psi_{[A]}(\epsilon_j,\alpha_j)$ with appreciable $P_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,t)$ are characterized by

$$
\epsilon_j\ll\left|\frac{d\ln\mathfrak{N}_{[B]}(E)/dE}{d^2\ln\mathfrak{N}_{[B]}(E)/dE^2}\right|\approx\left|\frac{d(E^{\text{const}})/dE}{d^2(E^{\text{const}})/dE^2}\right|\approx E\approx\eta_u\approx\eta_v.
$$

Equation (63) corresponds to the assignment of a canonical ensemble to the system of interest $[A]$ and of a microcanonical ensemble to the surroundings $[B]$ in the ultimate and time-persistent equilibrium statistical configuration of the supersystem $[A+B]$.

We now consider the case of the system of interest $[A]$ in nonequilibrium and the surroundings $[B]$ in equilibrium; physically this is possible only if $[A]$ is much smaller than $[B]$. Quantitatively, the assertion that $[B]$ is in equilibrium while $[A]$ is not, is equivalent to the statement that $P_{[A+B]}(\epsilon_j,\alpha_j;\eta_u,\beta_u;\,t)$ has the same numerical value for all $\beta_u:\beta_u(1),\,\beta_u(2),\,\cdots,\,\beta_u(n),\,\cdots,\,\beta_u[\mathfrak{N}_{[B]}(\eta_u)]$; this implies, using Eq. (55), that $P_{[B]}(\eta_u,\beta_u;\,t)$ also has the same numerical value for all β_u, consistent with the expression in Eq. (63) for $P_{[B]}{}^{\text{equil}}(\eta_u,\beta_u;\,t)$. With the $P_{[A+B]}(\epsilon_j,\alpha_j;\,\eta_u,\beta_u;\,t)$ the same for all β_u these $P_{[A+B]}(\epsilon_j,\alpha_j;\,\eta_u,\beta_u;\,t)$ cancel from numerator and denominator in the expressions on the right-hand side of Eq. (57) and the (in general, time-dependent) $w_{[A]}(\epsilon_j,\alpha_j;\,\epsilon_k,\alpha_k;\,t)$, $w_{[A]}(\epsilon_k,\alpha_k;\,\epsilon_j,\alpha_j;\,t)$ are equal to the time-independent $w_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,\epsilon_k,\alpha_k;\,t)$, $w_{[A]}{}^{\text{equil}}(\epsilon_k,\alpha_k;\,\epsilon_j,\alpha_j;\,t)$ of Eqs. (61) and (62). The "master" equation for $P_{[A]}(\epsilon_j,\alpha_j;\,t)$, Eq. (56), then assumes the form:

$$
\begin{aligned}
\frac{d}{dt}P_{[A]}(\epsilon_j;\,\alpha_j;\,t)
&=\sum_{\epsilon_k,\alpha_k}[w_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,\epsilon_k,\,\alpha_k;\,t)P_{[A]}(\epsilon_k,\alpha_k;\,t)\\
&\qquad-w_{[A]}{}^{\text{equil}}(\epsilon_k,\alpha_k;\,\epsilon_j,\,\alpha_j;\,t)P_{[A]}(\epsilon_j,\,\alpha_j;\,t)],
\end{aligned}
\tag{64}
$$

with [see Eqs. (61), (60), (63), (62)]

$$
\begin{aligned}
w_{[A]}{}^{\text{equil}}&(\epsilon_j,\alpha_j;\,\epsilon_k,\alpha_k;\,t)\\
&\cong\frac{\sum_{\beta_u,\beta_v}W_{[A+B]}(\epsilon_j,\,\alpha_j;\,E-\epsilon_j,\,\beta_u;\,\epsilon_k,\,\alpha_k,\,E-\epsilon_k,\,\beta_v)}{\mathfrak{N}(e^{-\epsilon_k/\Theta}/\sum_{\epsilon_l,\alpha_l}e^{-\epsilon_l/\Theta})}\\
&=\sum_{\beta_u,\beta_v}W_{[A+B]}(\epsilon_j,\,\alpha_j,\,E-\epsilon_j,\,\beta_u;\,\epsilon_k,\,\alpha_k,\,E-\epsilon_k,\,\beta_v)\\
&\qquad\times e^{-(E-\epsilon_k)/\Theta}/\sum_{\eta_w,\beta_w}e^{-\eta_w/\Theta}\\
&=\sum_{\eta_u,\beta_u,\eta_v,\beta_v}W_{[A+B]}(\epsilon_j,\alpha_j,\eta_u,\beta_u;\,\epsilon_k,\alpha_k,\eta_v,\beta_v)\\
&\qquad\times e^{-\eta_v/\Theta}/\sum_{\eta_w,\beta_w}e^{-\eta_w/\Theta},
\end{aligned}
\tag{65}
$$

$$
\frac{w_{[A]}{}^{\text{equil}}(\epsilon_j,\alpha_j;\,\epsilon_k,\alpha_k;\,t)}{w_{[A]}{}^{\text{equil}}(\epsilon_k,\alpha_k;\,\epsilon_j,\alpha_j;\,t)}=\frac{P_{[A]}{}^{\text{equil}}(\epsilon_j,\,\alpha_j;\,t)}{P_{[A]}{}^{\text{equil}}(\epsilon_k,\,\alpha_k;\,t)}\cong\frac{e^{-\epsilon_j/\Theta}}{e^{-\epsilon_k/\Theta}},
$$

which can be employed to describe the approach of [A] to equilibrium (see Sec. D). The "master" equation for $P_{[B]}(\eta_u,\beta_u(n);t)$, Eq. (58), becomes, using Eqs. (59), (36)

$$\frac{d}{dt}P_{[B]}(\eta_u,\beta_u(n);t)=\sum_{\eta_v,\alpha_j,\alpha_k}[P_{[A+B]}(E-\eta_v,\alpha_k;\eta_v,\beta_v(n);t)-P_{[A+B]}(E-\eta_u,\alpha_j;\eta_u,\beta_u(n);t)]\times\sum_{m=1}^{\mathfrak{N}_{[B]}(\eta_v)}W_{[A+B]}(E-\eta_u,\alpha_j,\eta_u,\beta_u(n);E-\eta_v,\alpha_k,\eta_v,\beta_v(m))$$

$$\cong\sum_{\alpha_j,\alpha_k}[P_{[A+B]}(E-\eta_u,\alpha_j;\eta_u,\beta_u(n);t)-P_{[A+B]}(E-\eta_u,\alpha_j;\eta_u,\beta_u(n);t)]\times\sum_{m=1}^{\mathfrak{N}_{[B]}(\eta_u)}W_{[A+B]}(E-\eta_u,\alpha_j,\eta_u,\beta_u(n);E-\eta_u,\alpha_k,\eta_u,\beta_u(m))=0.$$

Thus $P_{[B]}(\eta_u,\beta_u(n);t)$ is time-persistent as is required by the circumstance that [B] is in equilibrium (though [A] is not).

We conclude this section with an illustration of the use of the "master" equation for $P_{[A]}(\epsilon_j,\alpha_j;t)$, Eqs. (64), (65), in the derivation of an entropy theorem for the system of interest [A]. We define the entropy of a system of interest [A] whose statistical configuration obeys such a "master" equation, as,

$$S_{[A]}(t)\equiv-k\sum_{\epsilon_j,\alpha_j}P_{[A]}(\epsilon_j,\alpha_j;t)\ln P_{[A]}(\epsilon_j,\alpha_j;t),\qquad(67)$$

and obtain from Eqs. (67), (64)

$$\frac{dS_{[A]}(t)}{dt}=(k/2)\sum_{\epsilon_j,\alpha_j,\epsilon_k,\alpha_k}[w_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;\epsilon_k,\alpha_k;t)\times P_{[A]}(\epsilon_k,\alpha_k;t)-w_{[A]}^{\text{equil}}(\epsilon_k,\alpha_k;\epsilon_j,\alpha_j;t)\times P_{[A]}(\epsilon_j,\alpha_j;t)]\times\ln[P_{[A]}(\epsilon_k,\alpha_k;t)/P_{[A]}(\epsilon_j,\alpha_j;t)],\qquad(68)$$

as the basic equation for the time rate of change of the entropy of [A] arising from: (1) the approach of the probabilities $P_{[A]}(\epsilon_j,\alpha_j;t)$ towards their ultimate and time-persistent equilibrium values $P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)$ without any net flow of heat between [B] and [A], and (2) from any net flow of heat between [B] and [A], $dQ_{[A]}/dt$. In this last connection, defining the internal energy of [A] as

$$U_{[A]}(t)\equiv\sum_{\epsilon_j,\alpha_j}P_{[A]}(\epsilon_j,\alpha_j;t)\epsilon_j,\qquad(69)$$

we have [again using Eq. (64)]

$$\frac{dU_{[A]}(t)}{dt}=\sum_{\epsilon_j,\alpha_j}\frac{dP_{[A]}(\epsilon_j,\alpha_j;t)}{dt}\epsilon_j-\sum_{\epsilon_j,\alpha_j}P_{[A]}(\epsilon_j,\alpha_j;t)\left(-\frac{\partial\epsilon_j(V_{[A]})}{\partial V_{[A]}}\right)\frac{dV_{[A]}}{dt}$$
$$=\tfrac{1}{2}\sum_{\epsilon_j,\alpha_j,\epsilon_k,\alpha_k}[w_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;\epsilon_k,\alpha_k;t)\times P_{[A]}(\epsilon_k,\alpha_k;t)-w_{[A]}^{\text{equil}}(\epsilon_k,\alpha_k;\epsilon_j,\alpha_j;t)\times P_{[A]}(\epsilon_j,\alpha_j;t)](\epsilon_j-\epsilon_k)-\sum_{\epsilon_j,\alpha_j}P_{[A]}(\epsilon_j,\alpha_j;t)\left(-\frac{\partial\epsilon_j(V_{[A]})}{\partial V_{[A]}}\right)\frac{dV_{[A]}}{dt}\qquad(70)$$
$$=\frac{dQ_{[A]}}{dt}-p_{[A]}\frac{dV_{[A]}}{dt},\text{[9]}$$

where it is clear that $dQ_{[A]}/dt$ may be either positive or negative depending on the direction of the net flow between [B] and [A], and in general, vanishes only in equilibrium—see Eqs. (62) or (65). These last equations, used in Eq. (68), also ensure the vanishing of $dS_{[A]}/dt$ in equilibrium.

We now define

$$\Delta(j;t)\equiv\frac{P_{[A]}(\epsilon_j,\alpha_j;t)-P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)}{P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)},\qquad(71)$$

which represents, at time t, the relative deviation of the probability $P_{[A]}(\epsilon_j,\alpha_j;t)$ from its equilibrium value $P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)$. Expression of $dQ_{[A]}/dt$, $dS_{[A]}/dt$ in terms of $\Delta(j;t)$ and

$$\lambda_{jk}\equiv w_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;\epsilon_k,\alpha_k;t)P_{[A]}^{\text{equil}}(\epsilon_k,\alpha_k;t)=w_{[A]}^{\text{equil}}(\epsilon_k,\alpha_k;\epsilon_j,\alpha_j;t)P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)$$

[see Eqs. (62) or (65)] yields,

$$\frac{dQ_{[A]}(t)}{dt}=\tfrac{1}{2}\sum_{j,k}\lambda_{jk}[\Delta(k;t)-\Delta(j;t)](\epsilon_j-\epsilon_k),\qquad(72)$$

$$\frac{dS_{[A]}(t)}{dt}=\frac{k}{2}\sum_{j,k}\lambda_{jk}[\Delta(k;t)-\Delta(j;t)]\ln\left(\frac{1+\Delta(k;t)}{1+\Delta(j;t)}\right)+\frac{k}{2}\sum_{j,k}\lambda_{jk}[\Delta(k;t)-\Delta(j;t)]\times\ln\left(\frac{P_{[A]}^{\text{equil}}(\epsilon_k,\alpha_k;t)}{P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)}\right),\qquad(73)$$

[9] $V_{[A]}$ is the volume of [A] and $p_{[A]}$ is the pressure exerted by [A] on [B]. $dV_{[A]}/dt$ is sufficiently slow so as not to induce any transitions between $\psi_{[A]}(\epsilon_j,\alpha_j)$ and $\psi_{[A]}(\epsilon_k,\alpha_k)$.

whence, using Eq. (63),

$$\frac{dS_{[A]}(t)}{dt}=\frac{k}{2}\sum_{j,k}\lambda_{jk}[\Delta(k;t)-\Delta(j;t)]\times\ln\left(\frac{1+\Delta(k;t)}{1+\Delta(j;t)}\right)+\frac{1}{T}\frac{dQ_{[A]}(t)}{dt}. \quad (74)$$

The first term on the right hand side of Eq. (74) is (except in equilibrium) always positive and represents the time rate of increase of the entropy of $[A]$ associated with the establishment, without any net heat flow between $[B]$ and $[A]$, of the ultimate and time-persistent equilibrium probability distribution $P_{[A]}^{\text{equil}}(\epsilon_j,\alpha_j;t)$ relative to the initial probability distribution $P_{[A]}(\epsilon_j,\alpha_j;t_0)$. On the other hand, the second term on the right hand side of Eq. (74) represents the time rate of increase or decrease of the entropy of $[A]$ associated with the direction of the net flow of heat between $[B]$ and $[A]$. Only under circumstances such that $dQ_{[A]}(t)/dt>0$ (net heat flow from $[B]$ to $[A]$) is $dS_{[A]}(t)/dt$ necessarily >0.

D. THE SOLUTION OF THE "MASTER" OR BOLTZMANN "GAIN-LOSS" EQUATION

For simplicity we rewrite the "master" or Boltzmann "gain-loss" equations (35), (64) in matrix form as:

$$\frac{d}{dt}\|P(t)\|=\|W\|\cdot\|P(t)\|,^{10} \quad (75)$$

where

$$\|W\|\equiv\begin{vmatrix}-(1/T_1) & W_{12} & \cdots & W_{1N}\\ W_{21} & -(1/T_2) & \cdots & W_{2N}\\ \vdots & \vdots & & \vdots\\ W_{N1} & W_{N2} & \cdots & -(1/T_N)\end{vmatrix}; \quad (76)$$

$$\|P(t)\|\equiv\begin{vmatrix}P(1;t)\\ P(2;t)\\ \vdots\\ P(N;t)\end{vmatrix};\quad N\equiv\mathfrak{N},$$

with

$$W_{nm}/W_{mn}=1\quad[\text{Eq. (36)}];$$
$$(1/T_n)\equiv\textstyle\sum_m W_{mn}(1-\delta_{mn})\quad[\text{Eq. (23)}, \quad (77)$$

for the supersystem $[A+B]$, and,

$$\frac{d}{dt}\|Q(t)\|=\|U\|\cdot\|Q(t)\|, \quad (78)$$

[10] In the mathematics literature a "master" equation of the form of Eq. (75) is known as a "Markoff chain" equation in a continuous variable. For a discussion of general methods of solution of "Markoff chain" equations see J. S. Doob, *Stochastic Processes* (John Wiley & Sons, New York, 1953); W. Feller, *Introduction to Probability Theory* (John Wiley & Sons, New York, 1957); W. Ledermann, Proc. Cambridge Phil. Soc. **46**, 581 (1950); **47**, 626 (1951). The solution of "master" type equations is worked out for various special cases in the physics literature, e.g., N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948); J. P. Lloyd and G. E. Pake, Phys. Rev. **94**, 579 (1954); F. Lurcat, Compt. rend. **238**, 1386 (1954); **238**, 2517 (1954); I. Solomon, Phys. Rev. **99**, 559 (1955).

where[11]

$$\|U\|\equiv\begin{vmatrix}-(1/T_1) & U_{12} & \cdots & U_{1N}\\ U_{21} & -(1/T_2) & \cdots & U_{2N}\\ \vdots & \vdots & & \vdots\\ U_{N1} & U_{N2} & \cdots & -(1/T_N)\end{vmatrix};$$

$$U_{12}\equiv W(1,2)e^{[E(1)-E(2)]/2kT},\ \cdots,$$
$$U_{rs}\equiv W(r,s)e^{[E(r)-E(s)]/2kT},\ \cdots, \quad (79)$$

$$\|Q(t)\|\equiv\begin{vmatrix}Q(1;t)\\ Q(2;t)\\ \vdots\\ Q(N;t)\end{vmatrix}\equiv\begin{vmatrix}P(1;t)e^{E(1)/2kT}\\ P(2;t)e^{E(2)/2kT}\\ \vdots\\ P(N;t)e^{E(N)/2kT}\end{vmatrix},$$

with

$$E(1)\equiv\epsilon_1,\ \cdots,\quad E(\mathfrak{N}_{[A]}(\epsilon_1))\equiv\epsilon_1,$$
$$E(\mathfrak{N}_{[A]}(\epsilon_1)+1)\equiv\epsilon_2,\ \cdots;$$
$$W(1,2)\equiv w_{[A]}^{\text{equil}}(\epsilon_1,\alpha_1(1);\epsilon_1,\alpha_1(2);t),\ \cdots,$$
$$W(1;\mathfrak{N}_{[A]}(\epsilon_1)+1)$$
$$\equiv w_{[A]}^{\text{equil}}(\epsilon_1,\alpha_1(1);\epsilon_2,\alpha_2(1);t),\ \cdots;$$
$$P(1;t)\equiv P_{[A]}(\epsilon_1,\alpha_1(1);t),\ \cdots,$$
$$P(\mathfrak{N}_{[A]}(\epsilon_1)+1;t)\equiv P_{[A]}(\epsilon_2,\alpha_2(1);t),\ \cdots; \quad (80)$$
$$N\equiv\mathfrak{N}_{[A]}\equiv\sum_{\epsilon_j}\mathfrak{N}_{[A]}(\epsilon_j);$$
$$\frac{U_{rs}}{U_{sr}}\equiv\frac{W(r,s)e^{[E(r)-E(s)]/2kT}}{W(s,r)e^{[E(s)-E(r)]/2kT}}=1\quad[\text{Eq. (65)}];$$
$$(1/T_r)\equiv\sum_s W(s,r)(1-\delta_{sr})$$

for the system of interest $[A]$. Since $\|W\|$ and $\|U\|$ are both symmetric matrices, Eqs. (75)–(77) are of the the same general form as Eqs. (78)–(80), and it will suffice to discuss the solutions of the former, those of the latter being obtainable from those of the former by appropriate substitutions.

The solution of Eqs. (75)–(77) can now be written as

$$\|P(t)\|=\sum_{\nu=0}^{N-1}(\|\tilde{p}_\nu\|\cdot\|P(t_0\|)\|p_\nu\|e^{-\omega_\nu(t-t_0)};$$
$$\|p_\nu\|\equiv\begin{vmatrix}p_\nu(1)\\ p_\nu(2)\\ \vdots\\ p_\nu(N)\end{vmatrix}, \quad (81)$$

with

$$(-\|W\|)\cdot\|p_\nu\|=\omega_\nu\|p_\nu\|;\quad\|\tilde{p}_\sigma\|\cdot\|p_\nu\|=\delta_{\sigma\nu}, \quad (82)$$

the ω_ν, $\|p_\nu\|$ being the eigenvalues (here assumed nondegenerate) and the corresponding eigenvectors of the

[11] The relationship between $Q(r;t)$ and $P(r;t)$ used in Eq. (79) was suggested to us by Professor F. Bloch. See also E. W. Montroll and K. W. Shuler, *Advances in Chemical Physics* (Interscience Publishers, New York, 1958), Vol. 1, p. 361.

matrix $-\|W\|$. Since $-\|W\|$ is symmetric—"microscopic reversibility," Eqs. (36), (77)—the ω_ν:

$$\omega_0<\omega_1<\omega_2<\cdots<\omega_{N-1}$$

are all *real*, while the normalizability of the $P(n;t)$ for all t $[(d/dt)\sum_n P(n;t)=0$ or $\sum_n P(n;t)=1]$ demands that the algebraically smallest ω_ν is zero, i.e.,

$$0=\omega_0<\omega_1<\omega_2<\cdots<\omega_{N-1}.^{12} \tag{83}$$

Thus, substituting Eq. (83) into Eqs. (81), (89)

$$\|P(t)\|=(\|\tilde{p}_0\|\cdot\|P(t_0)\|)\|p_0\| + \sum_{\nu=1}^{N-1}(\|\tilde{p}_\nu\|\cdot\|P(t_0)\|)\|p_\nu\|e^{-\omega_\nu(t-t_0)} \tag{84}$$

$$=\|P^{\text{equil}}\|+\sum_{\nu=1}^{N-1}(\|\tilde{p}_\nu\|\cdot\|P(t_0)\|)\|p_\nu\|e^{-\omega_\nu(t-t_0)},$$

$$(-\|W\|)\cdot\|p_0\|=0, \tag{85}$$

and, since the $\|W\|$ of Eqs. (76), (77) satisfies,

$$(-\|W\|)\cdot\|1\|=(-\|\tilde{W}\|)\cdot\|1\|=0, \tag{86}$$

we have (ω_0 assumed nondegenerate!)

$$\|p_0\|=(1/\mathfrak{N}^{\frac{1}{2}})\|1\|. \tag{87}$$

Hence, from Eqs. (84), (87)

$$\|P^{\text{equil}}\|=(1/\mathfrak{N})(\textstyle\sum_n P(n;t_0))\|1\|=(1/\mathfrak{N})\|1\| \tag{88}$$

in agreement with Eq. (41) or Eq. (50), The reality of the various ω_ν in Eq. (81) or (84) shows in addition that $\|P(t)\|$ approaches $\|P^{\text{equil}}\|$ in a nonoscillatory fashion, the $(\omega_1)^{-1}$, $(\omega_2)^{-1}$, $\cdots$, $(\omega_{N-1})^{-1}$ playing the role of relaxation times. Similarly, solution of Eqs. (78)–(80) yields,

$$\|Q(t)\|=\sum_{\nu=0}^{N-1}(\|\tilde{q}_\nu\|\cdot\|Q(t_0)\|)\|q_\nu\|e^{-\omega_\nu'(t-t_0)}$$

$$=(\|\tilde{q}_0\|\cdot\|Q(t_0)\|)\|q_0\| + \sum_{\nu=1}^{N-1}(\|\tilde{q}_\nu\|\cdot\|Q(t_0)\|)\|q_\nu\|e^{-\omega_\nu'(t-t_0)} \tag{89}$$

$$=\|Q^{\text{equil}}\|+\sum_{\nu=1}^{N-1}(\|\tilde{q}_\nu\|\cdot\|Q(t_0)\|)\|q_\nu\|e^{-\omega_\nu'(t-t_0)},$$

with

$$(-\|U\|)\cdot\|q_\nu\|=\omega_\nu'\|q_\nu\|;\quad \|\tilde{q}_\sigma\|\cdot\|q_\nu\|=\delta_{\sigma\nu}, \tag{90}$$

and

$$(-\|U\|)\cdot\|q_0\|=\omega_0'\|q_0\|=0, \tag{91}$$

whence, with the $\|U\|(=\|\tilde{U}\|)$ of Eqs. (79), (80),

$$\|q_0\|=\frac{1}{Z_{[A]}^{\frac{1}{2}}}\begin{vmatrix} e^{-E(1)/2kT} \\ e^{-E(2)/2kT} \\ \vdots \\ e^{-E(N)/2kT}\end{vmatrix};\quad Z_{[A]}\equiv\sum_r e^{-E(r)/kT}\equiv\sum_{\epsilon_j,\alpha_j}e^{-\epsilon_j/kT}, \tag{92}$$

so that, substituting into Eq. (89)

$$\|Q^{\text{equil}}\|=\frac{(\sum_r P(r;t_0))}{Z_{[A]}}\begin{vmatrix} e^{-E(1)/2kT} \\ e^{-E(2)/2kT} \\ \vdots \\ e^{-E(N)/2kT}\end{vmatrix} =\frac{1}{Z_{[A]}}\begin{vmatrix} e^{-E(1)/kT}\cdot e^{E(1)/2kT} \\ e^{-E(2)/kT}\cdot e^{E(2)/2kT} \\ \vdots \\ e^{-E(N)/kT}\cdot e^{E(N)/2kT}\end{vmatrix}, \tag{93}$$

i.e., using Eqs. (80), (79),

$$P_{[A]}^{\text{equil}}(\epsilon_1,\alpha_1(1);t)\equiv P^{\text{equil}}(1;t)\equiv Q^{\text{equil}}(1)e^{-E(1)/2kT} =(e^{-\epsilon_1/kT}/\sum_{\epsilon_j,\alpha_j}e^{-\epsilon_j/kT}),\quad\text{etc.,} \tag{94}$$

in agreement with Eq. (63). The symmetry of $-\|U\|$—"detailed balance," Eqs. (62), (65), (80)—ensures the reality of the ω_ν' and so the nonoscillatory character of the approach of $\|Q(t)\|$ to $\|Q^{\text{equil}}\|$.

An interesting lower limit can be obtained for the shortest of the relaxation times, i.e., for $(\omega_{N-1})^{-1}$, viz.,

$$(\tfrac{1}{2})T(\min)\leqq(\omega_{N-1})^{-1};\quad T(\min)\equiv\text{smallest of the } T_n, \tag{95}$$

so that the shortest relaxation time is $\geqq\frac{1}{2}$ (lifetime of the shortest lived state). Equation (95) follows upon introduction of the "non-negative" symmetric matrix,

$$\|X\|\equiv\frac{1}{T(\min)}\|1\|+\|W\|=\begin{vmatrix} [1/T(\min)-1/T_1] & W_{12} & \cdots & W_{1N} \\ W_{21} & [1/T(\min)-1/T_2] & \cdots & W_{2N} \\ \vdots & \vdots & & \vdots \\ W_{N1} & W_{N2} & \cdots & [1/T(\min)-1/T_N]\end{vmatrix}, \tag{96}$$

$$X_{11}=[1/T(\min)-1/T_1]\geqq0,\quad X_{12}=W_{12}\geqq0,\quad\text{etc.,}$$

[12] The normalizability of the $P(n;t)$ for all t, as given, e.g., in Eq. (4), is also obtainable from Eq. (11) since, on the basis of Eq. (9) or Eq. (14), $\sum_n Y_n(\tau;t-t_0)=0$ and since $\sum_{nm}[W_{nm}(\tau)P(m;t)-W_{mn}(\tau)P(n;t)]=0$. Thus the neglect of $Y_n(\tau;t-t_0)$ in passing from the rigorous Eq. (11) to the approximate Eq. (35) (the "master" or Boltzmann "gain-loss" type equation) does not upset the normalizability of the $P(n;t)$. From a mathematical point of view, the normalizability of the $P(n;t)$ in Eq. (35) is a consequence of the fact that each column of the $-\|W\|$ matrix vanishes, and this property of $-\|W\|$ together with Eq. (82) may be used directly to establish Eq. (83) and also Eq. (87) below.

and use of a theorem of Frobenius[13] to the effect that a non-negative symmetric matrix such as $\|X\|$ has an eigenvalue spectrum x_ν: $x_0 \geqq x_1 \geqq x_2 \geqq \cdots \geqq x_{N-1}$ such that

$$x_0 \geqq x_1 \geqq x_2 \geqq \cdots \geqq x_p \geqq 0 \geqq x_{p+1} \geqq \cdots \geqq x_{N-1}, \quad (97)$$

and

$$x_0 \geqq |x_{N-1}|. \quad (98)$$

Equations (98), (96), and (75) yield

$$[1/T(\min)] \geqq |[1/T(\min)] - \omega_{N-1}|, \quad (99)$$

which, upon squaring and dividing by ω_{N-1}, is seen to be equivalent to Eq. (95).[14] On the other hand, no general expression in terms of the T_n seems to exist for the upper limit to the longest of the relaxation times, $(\omega_1)^{-1}$, though examination of particular examples (see Sec. F) appears to indicate that, as might be expected physically,

$$(\omega_1)^{-1} \approx T(\max);\quad T(\max) \equiv \text{largest of the } T_n. \quad (100)$$

As an example, we shall now give an explicit expression for $\|Q(t)\|$ in the simplest case: $N=2$. Here, from Eqs. (79), (80), (92), (90), (93), we have

$$\begin{aligned}
\|U\| &= \begin{vmatrix} -W(2,1) & W(1,2)e^{[E(1)-E(2)]/kT} \\ W(2,1)e^{[E(2)-E(1)]/kT} & -W(1,2) \end{vmatrix}; \\
\|q_0\| &= \frac{1}{Z_{[A]}^{\frac{1}{2}}} \begin{vmatrix} e^{-E(1)/2kT} \\ e^{-E(2)/2kT} \end{vmatrix} = \frac{1}{(e^{-E(1)/kT}+e^{-E(2)/kT})^{\frac{1}{2}}} \begin{vmatrix} e^{-E(1)/2kT} \\ e^{-E(2)/2kT} \end{vmatrix}; \\
\|q_1\| &= \frac{1}{Z_{[A]}^{\frac{1}{2}}} \begin{vmatrix} e^{-E(2)/2kT} \\ -e^{-E(1)/2kT} \end{vmatrix}; \quad \omega_1' = W(1,2)+W(2,1); \\
\|Q^{\text{equil}}\| &= \frac{1}{Z_{[A]}} \begin{vmatrix} e^{-E(1)/kT} \cdot e^{E(1)/2kT} \\ e^{-E(2)/kT} \cdot e^{E(2)/2kT} \end{vmatrix},
\end{aligned} \quad (101)$$

so that from Eqs. (101), (89), (79),

$$\begin{aligned}
\|Q(t)\| &= \begin{vmatrix} P(1;t)e^{E(1)/2kT} \\ P(2;t)e^{E(2)/2kT} \end{vmatrix} \\
&= \frac{1}{Z_{[A]}} \begin{vmatrix} e^{-E(1)/kT} \cdot e^{E(1)/2kT} \\ e^{-E(2)/kT} \cdot e^{E(2)/2kT} \end{vmatrix} + \frac{1}{Z_{[A]}} [P(1;t_0)e^{[E(1)-E(2)]/2kT} - P(2;t_0)e^{-[E(1)-E(2)]/2kT}] \\
&\qquad \times \begin{vmatrix} e^{-E(2)/2kT} \\ e^{-E(1)/2kT} \end{vmatrix} e^{-[W(1,2)+W(2,1)](t-t_0)},
\end{aligned} \quad (102)$$

i.e., using also Eq. (80)

$$\begin{aligned}
P(1;t) &= (1/Z_{[A]})e^{-E(1)/kT} + (1/Z_{[A]})[e^{-E(2)/kT}P(1;t_0) - e^{-E(1)/kT}P(2;t_0)]e^{-[W(1,2)+W(2;1)](t-t_0)} \\
&= \frac{W(1,2)}{W(1,2)+W(2,1)} + \left(\frac{W(2,1)P(1;t_0) - W(1,2)P(2;t_0)}{W(1,2)+W(2,1)}\right) e^{-[W(1,2)+W(2;1)](t-t_0)}, \\
P(2;t) &= (1/Z_{[A]})e^{-E(2)/kT} - (1/Z_{[A]})[e^{-E(2)/kT}P(1;t_1) - e^{-E(1)/kT}P(2;t_0)]e^{-W(1,2)+W(2,1)](t-t_0)} \\
&= \frac{W(2,1)}{W(1,2)+W(2,1)} - \left(\frac{W(2,1)P(1;t_0) - W(1;2)P(2;t_0)}{W(1,2)+W(2,1)}\right) e^{-[W(1,2)+W(2,1)](t-t_0)}.
\end{aligned} \quad (103)$$

Equation (103) demonstrates the proportionality of $P(1;t) - P^{\text{equil}}(1;t)$, $P(2;t) - P^{\text{equil}}(2;t)$ to

$$\begin{aligned}
&\pm[W(2,1)P(1;t_0) - W(1,2)P(2;t_0)] \\
&\quad = \pm\{W(2,1)[P(1;t_0) - P^{\text{equil}}(1;t)] \\
&\qquad - W(1,2)[P(2;t_0) - P^{\text{equil}}(2;t)]\}
\end{aligned}$$

[see Eq. (65)], i.e., to the initial deviation from "detailed balance" and so to the initial deviation from equilibrium.

In concluding this section we wish to point out that

[13] See, for example, E. Bodewig, *Matrix Calculus* (North Holland Publishing Company, Amsterdam, 1956), p. 145.

[14] The method of proof of Eq. (95) given in Eqs. (96)–(99) was suggested to us by Professor I. I. Hirschman. For nondegenerate ω_ν, the $\geqq$, $\leqq$ signs in Eq. (99), (95) must be replaced by $>$, $<$ signs. Our statement of Frobenius' theorem is valid only for a non-negative symmetric matrix $\|X\|$. The theorem can also be proved for any non-negative matrix, in which case some of the x_j with $1 \leqq j \leqq N-1$ may be complex, and Eqs. (97), (98) become: $x_0 \geqq |x_1| \geqq \cdots \geqq |x_{N-1}|$.

a Laplace transform method for solving Eqs. (75)–(77) or (78)–(80) yields an explicit formula for the matrix $\|K_\nu\| \equiv (\|\tilde{p}_\nu\| \cdot \|P(t_0)\|)\|p_\nu\|$ in Eq. (81) or for the analogous $\|K_\nu'\| \equiv (\|\tilde{q}_\nu\| \cdot \|Q(t_0)\|)\|q_\nu\|$ in Eq. (89), viz.,

$$\|K_\nu\| = (\|\tilde{p}_\nu\| \cdot \|P(t_0)\|)\|p_\nu\| = \left[\frac{1}{\dfrac{dD(s)}{ds}}\right] \begin{vmatrix} C(1;s) \\ C(2;s) \\ \vdots \\ C(N;s) \end{vmatrix}_{s=-\omega_\nu}, \tag{104}$$

where

$$D(s) \equiv \det(s\|1\| - \|W\|), \tag{105}$$

$C(n;s) \equiv$ same determinant as $D(s)$ but with nth column replaced by

$$\begin{vmatrix} P(1;t_0) \\ P(2;t_0) \\ \vdots \\ P(N;t_0) \end{vmatrix}.$$

Equations (104) and (105) are valid for nondegenerate ω_ν and are derived in Appendix B below; the corresponding equations for degenerate ω_ν are also given in this Appendix. It is to be noted for future reference that, from Eqs. (104), (87), (82),

$$\textstyle\sum_n K_0(n) = (\|\tilde{p}_0\| \cdot \|P(t_0)\|)\sum_n p_0(n) = \sum_n P(n;t_0) = 1, \tag{106}$$

$$\begin{aligned}\textstyle\sum_n K_\nu(n) &= (\|\tilde{p}_\nu\| \cdot \|P(t_0)\|)\textstyle\sum_n p_\nu(n) \qquad (1 \leqq \nu \leqq N-1) \\ &= (\|\tilde{p}_\nu\| \cdot \|P(t_0)\|)\mathfrak{N}^{\frac{1}{2}}(\|\tilde{p}_\nu\| \cdot \|p_0\|) = 0.\end{aligned} \tag{107}$$

E. THE "MASTER" OR BOLTZMANN "GAIN-LOSS" EQUATION FOR AN INDIVIDUAL PARTICLE OR QUASI-PARTICLE OF THE SYSTEM OF INTEREST

If the states $\psi_{[A]}(\epsilon_j,\alpha_j)$ of the system of interest $[A]$ can be appropriately described in terms of the states $\psi_{[1]}(j^{(1)}), \psi_{[2]}(j^{(2)}), \cdots, \psi_{[i]}(j^{(i)}), \cdots, \psi_{[q]}(j^{(q)}), \cdots$ of its constituent individual particles or quasi-particles $[1], [2], \cdots [i], \cdots, [q], \cdots$, we can consider

$$\begin{gathered} P_{[A]}(\epsilon_j,\alpha_j;t) \equiv P_{[A]}(\{j^{(i)}\};t); \\ \epsilon_j,\, \alpha_j \equiv \epsilon(\{j^{(i)}\}), \alpha(\{j^{(i)}\}); \\ \{j^{(i)}\} \equiv j^{(1)}, j^{(2)}, \cdots, j^{(i)}, \cdots, j^{(q-1)}, j^{(q)}, j^{(q+1)}, \cdots \end{gathered} \tag{108}$$

as the joint probability that $[1], [2], \cdots, [i], \cdots, [q-1], [q], [q+1], \cdots$ are found in the states $\psi_{[1]}(j^{(1)}), \psi_{[2]}(j^{(2)}), \cdots, \psi_{[i]}(j^{(i)}), \cdots, \psi_{[q-1]}(j^{(q-1)}), \psi_{[q]}(j^{(q)}), \psi_{[q+1]}(j^{(q+1)}), \cdots$ at time t, equal identically to the probability that $[A]$ is found in the state $\psi_{[A]}(\epsilon_j,\alpha_j)$ at time t. We further define

$$\begin{gathered} P_{[q]}(j^{(q)};t) \equiv \sum_{\{j^{(i)}\}^{(q)}} P_{[A]}(\{j^{(i)}\};t); \\ \{j^{(i)}\}^{(q)} \equiv j^{(1)}, j^{(2)}, \cdots, j^{(i)}, \cdots, j^{(q-1)}, j^{(q+1)}, \cdots \end{gathered} \tag{109}$$

as the probability at time t that $[q]$ is found in the state $\psi_{[q]}(j^{(q)})$ for any probability distribution of $[1], [2], \cdots, [i], \cdots, [q-1], [q+1], \cdots$ over the various states $\psi_{[1]}(j^{(1)}), \psi_{[2]}(j^{(2)}), \cdots, \psi_{[i]}(j^{(i)}), \cdots, \psi_{[q-1]}(j^{(q-1)}), \psi_{[q+1]}(j^{(q+1)}), \cdots$. The "master" equation for

$$P_{[A]}(\{j^{(i)}\};t),$$

Eq. (64), together with Eq. (109), then yields

$$\frac{d}{dt}P_{[q]}(j^{(q)};t) = \sum_{k^{(q)}} [w_{[q]}(j^{(q)};k^{(q)};t)P_{[q]}(k^{(q)};t) - w_{[q]}(k^{(q)};j^{(q)};t)P_{[q]}(j^{(q)};t)], \tag{110}$$

with the, in general, time-dependent transition probabilities per unit time,

$$\begin{aligned} w_{[q]}(j^{(q)};k^{(q)};t) &= \frac{\displaystyle\sum_{\{j^{(i)}\}^{(q)},\,\{k^{(i)}\}^{(q)}} w_{[A]}{}^{\text{equil}}(\{j^{(i)}\},\{k^{(i)}\};t)P_{[A]}(\{k^{(i)}\};t)}{\displaystyle\sum_{\{k^{(i)}\}^{(q)}} P_{[A]}(\{k^{(i)}\};t)}, \\ w_{[q]}(k^{(q)};j^{(q)};t) &= \frac{\displaystyle\sum_{\{j^{(i)}\}^{(q)},\,\{k^{(i)}\}^{(q)}} w_{[A]}{}^{\text{equil}}(\{k^{(i)}\};\{j^{(i)}\};t)P_{[A]}(\{j^{(i)}\};t)}{\displaystyle\sum_{\{j^{(i)}\}^{(q)}} P_{[A]}(\{j^{(i)}\};t)} \end{aligned} \tag{111}$$

Let us now suppose that the system of interest $[A]$ is, as a whole, never too far from equilibrium so that we can replace the $P_{[A]}(\{j^{(i)}\};t)$ in Eq. (111) by their equilibrium values:

$$\begin{aligned} P_{[A]}{}^{\text{equil}}(\{j^{(i)}\};t) &\cong \frac{\exp[-\epsilon(\{j^{(i)}\})/\Theta]}{\displaystyle\sum_{\{k^{(i)}\}} \exp[-\epsilon(\{k^{(i)}\})/\Theta]} \quad \text{[Eqs. (63), (108)]}, \\ P_{[q]}{}^{\text{equil}}(j^{(q)};t) &= \sum_{\{j^{(i)}\}^{(q)}} P_{[A]}{}^{\text{equil}}(j^{(i)};t) \cong \frac{\displaystyle\sum_{\{j^{(i)}\}^{(q)}} \exp[-\epsilon(\{j^{(i)}\})/\Theta]}{\displaystyle\sum_{\{k^{(i)}\}} \exp[-\epsilon(\{k^{(i)}\})/\Theta]} \quad \text{[Eq. (109)]}. \end{aligned} \tag{112}$$

Then

$$w_{[q]}(j^{(q)};k^{(q)};t),\quad w_{[q]}(k^{(q)};j^{(q)};t)$$

are replaced by time-independent

$$w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t),\quad w_{[q]}{}^{\text{equil}}(k^{(q)};j^{(q)};t)$$

while Eq. (65)—"detailed balance"—ensures that the numerators in the two resultant expressions on the right-hand side of Eq. (111) are equal; thus, using also Eqs. (109), (112), we obtain

$$\frac{w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t)}{w_{[q]}{}^{\text{equil}}(k^{(q)},j^{(q)};t)}=\frac{\sum_{\{j^{(i)}\}(q)} P_{[A]}{}^{\text{equil}}(\{j^{(i)}\};t)}{\sum_{\{k^{(i)}\}(q)} P_{[A]}{}^{\text{equil}}(\{k^{(i)}\};t)}$$

$$=\frac{P_{[q]}{}^{\text{equil}}(j^{(q)};t)}{P_{[q]}{}^{\text{equil}}(k^{(q)};t)}\cong\frac{\sum_{\{j^{(i)}\}(q)}\exp[-\epsilon(\{j^{(i)}\})/\Theta]}{\sum_{\{k^{(i)}\}(q)}\exp[-\epsilon(\{k^{(i)}\})/\Theta]}. \tag{113}$$

Equation (110) with

$$w_{[q]}(j^{(q)},k^{(q)};t),\quad w_{[q]}(k^{(q)},j^{(q)};t)$$

replaced by

$$w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t),\quad w_{[q]}{}^{\text{equil}}(k^{(q)},j^{(q)};t)$$

and Eqs. (111)–(113) define the "master" equation for the particle or quasi-particle $[q]$; the analogy between these equations and the Eqs. (64), (65), defining the "master" equation for the system of interest $[A]$ is obvious, and we can use the methods of Sec. D to obtain $P_{[q]}(j^{(q)};t)$ as a function of t. A particular simplification is obtained if, to a sufficient approximation, $\epsilon(\{j^{(i)}\})$ depends additively on the $\epsilon_{[i]}(j^{(i)})$,

$$\begin{aligned}\epsilon(\{j^{(i)}\})\cong&\,\epsilon_{[1]}(j^{(1)})+\epsilon_{[2]}(j^{(2)})+\cdots\\&+\epsilon_{[i]}(j^{(i)})+\cdots+\epsilon_{[q-1]}(j^{(q-1)})\\&+\epsilon_{[q]}(j^{(q)})+\epsilon_{[q+1]}(j^{(q+1)})+\cdots,\end{aligned}\tag{114}$$

since Eqs. (114), (113) give

$$\frac{w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t)}{w_{[q]}{}^{\text{equil}}(k^{(q)};j^{(q)};t)}\cong\frac{\exp[-\epsilon_{[q]}(j^{(q)})/\Theta]}{\exp[-\epsilon_{[q]}(k^{(q)})/\Theta]} \tag{115}$$

in complete analogy with Eq. (65).

F. MAGNETIC RESONANCE: TIME VARIATION OF LONGITUDINAL MAGNETIZATION

We proceed to discuss certain magnetic resonance situations in view of the general theory established in Secs. B–E above. In these magnetic resonance situations, the system of interest $[A]$ is identified with the degrees of freedom describing the orientations of nuclear (or electronic) spins, and the surroundings $[B]$ with the degrees of freedom describing the motions of atoms containing the spins, i.e., in brief, $[A]\equiv$spins, $[B]\equiv$"lattice." The ratio

$$\mathcal{V}/\mathcal{H}^{(0)}=\mathcal{V}/(\mathcal{H}_{[A]}{}^{(0)}+\mathcal{H}_{[B]}{}^{(0)})$$

is now no longer $\approx N_{[A]}{}^{\frac{1}{2}}/(N_{[A]}+N_{[B]})$ but is independent of $N_{[A]}(=N_{[B]})$ and is not necessarily negligible for a sufficiently large specimen—on the other hand, $\mathcal{V}/\mathcal{H}^{(0)}$ is indeed small in many cases, e.g., for $\mathcal{V}\equiv$nonsecular spin-lattice phonon interaction (magnetic dipole-dipole or electric quadrupole spin-lattice interaction). We present a treatment of the approach of the nuclear spin system ($[A]$) toward equilibrium under circumstances in which the "lattice" ($[B]$) remains in equilibrium throughout and with $\mathcal{V}/(\mathcal{H}_{[A]}{}^{(0)}+\mathcal{H}_{[B]}{}^{(0)})$ small. Under these circumstances the conditions for validity of the "master" equations deduced in Secs. B, C, E are satisfied and our discussion is, in particular, based on the individual particle "master" equation of Sec. E.

We treat this "master" equation for an individual particle $[q]$, i.e., for an individual spin $[q]$, of the system of interest $[A]$, Eq. (110), with $w_{[q]}(j^{(q)};k^{(q)};t)$ $w_{[q]}(k^{(q)};j^{(q)};t)$ replaced by $w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t)$, $w_{[q]}{}^{\text{equil}}(k^{(q)};j^{(q)};t)$ and with Eqs. (111)–(113) for $w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t)$, $w_{[q]}{}^{\text{equil}}(k^{(q)};j^{(q)};t)$. These last equations, together with Eq. (65), yield

$$w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t)=\sum_{\{j^{(i)}\}(q),\,\{k^{(i)}\}(q),\,\eta_u,\beta_u,\eta_v,\beta_v}\left\{W_{[A+B]}(\{j^{(i)}\},\eta_u,\beta_u;\{k^{(i)}\},\eta_v,\beta_v)\frac{e^{-\eta_v/\Theta}}{\sum_{\eta_w,\beta_w}e^{-\eta_w/\Theta}}\right\}\times\left(\frac{\exp[-\epsilon(\{k^{(i)}\})/\Theta]}{\sum_{\{k^{(i)}\}(q)}\exp[-\epsilon(\{k^{(i)}\}/\Theta]}\right), \tag{116}$$

$$w_{[q]}{}^{\text{equil}}(k^{(q)};j^{(q)};t)=w_{[q]}{}^{\text{equil}}(j^{(q)};k^{(q)};t)\frac{\sum_{\{k^{(i)}\}(q)}\exp[-\epsilon(\{k^{(i)}\})/\Theta]}{\sum_{\{j^{(i)}\}(q)}\exp[-\epsilon(\{j^{(i)}\})/\Theta]},$$

where in the present instance $j^{(q)}$ is to be interpreted as the magnetic or spin-orientation quantum number of the spin $[q]$. Also, from Eq. (36),

$$\begin{aligned}W_{[A+B]}(\{j^{(i)}\},\eta_u,\beta_u;\{k^{(i)}\},\eta_v,\beta_v)&=(2\pi/\hbar)\delta(\epsilon(\{j^{(i)}\})+\eta_u-\epsilon(\{k^{(i)}\})-\eta_v)\,|\langle\{j^{(i)}\},\eta_u,\beta_u|\mathcal{V}|\{k^{(i)}\},\eta_v,\beta_v\rangle|^2\\&=W_{[A+B]}(\{k^{(i)}\},\eta_v,\beta_v;\{j^{(i)}\};\eta_u,\beta_u),\end{aligned}\tag{117}$$

where, for the case of the magnetic dipole-dipole spin-lattice interaction, $\mathcal{V}=\mathcal{V}_{\text{dip-dip}}$ and $\mathcal{V}_{\text{dip-dip}}$ can be identified with

$$\mathcal{V}_{\text{dip-dip}}{}^{\text{nonsecular}}=\tfrac{1}{2}\sum_{f,g}[C_{fg}(I_{[f]z}I_{[g]+}+I_{[f]+}I_{[g]z})+E_{fg}(I_{[f]+}I_{[g]+})]+\text{Herm. conj.},$$
$$C_{fg}\equiv-\frac{3}{2}\frac{\hbar^2\gamma^2}{(r_{fg})^3}\sin\theta_{fg}\cos\theta_{fg}e^{-i\phi_{fg}};\quad E_{fg}\equiv-\frac{3}{4}\frac{\hbar^2\gamma^2}{(r_{fg})^3}(\sin\theta_{fg})^2e^{-2i\phi_{fg}},\tag{118}$$

where $\gamma\equiv$nuclear gyromagnetic ratio;

$$\mathbf{r}_f-\mathbf{r}_g\equiv(r_{fg},\theta_{fg},\phi_{fg});\quad \mathbf{r}_f=\mathbf{R}_f+\boldsymbol{\xi}_f,$$

$\mathbf{R}_f\equiv$lattice vector of the atom $[f]$, $\boldsymbol{\xi}_f\equiv$displacement of the atom $[f]$ from its lattice position=function of phonon creation and destruction operators, and $\mathbf{I}_{[f]}\equiv$spin of the nucleus in the atom $[f]$. The term $\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}$ which establishes relatively rapidly a "quasi-equilibrium" spin configuration within $[A]$, need not be explicitly considered in the treatment of the relatively slower approach to equilibrium of dynamical variables such as the longitudinal magnetization since this relatively slower approach to equilibrium involves energy interchanges between the spins $[A]$ and the "lattice" $[B]$. If the atomic motions of the "lattice" $[B]$ are appropriate to, e.g., liquid-like rather than solid-like states of the specimen, $\mathbf{r}_f$ must be expressed in terms of creation and destruction operators of motional quasi-particles other than phonons. The general formalism developed below holds however in this case also.

We now introduce the notation $j^{(i)}\equiv m_i$, $k^{(i)}\equiv m_i'$ $(-I\leqq m_i, m_i'\leqq I)$ and find from Eq. (118) as typical nonvanishing matrix elements,

$$\langle\{m_i\}=\{m_i\}^{(q)},m_q;\eta_u,\beta_u|\mathcal{V}_{\text{dip-dip}}{}^{\text{nonsecular}}|\{m_i'\}=\{m_i\}^{(q)},m_q-1;\eta_v,\beta_v\rangle$$
$$=\sum_f\langle\eta_u,\beta_u|C_{fq}|\eta_v,\beta_v\rangle m_f[(I-m_q+1)(I+m_q)]^{\frac{1}{2}},\tag{119}$$

$$\langle\{m_i\}=\{m_i\}^{(q)\,(p)}m_q,m_p;\eta_u,\beta_u|\mathcal{V}_{\text{dip-dip}}{}^{\text{nonsecular}}|\{m_i'\}=\{m_i\}^{(q)\,(p)},m_q-1,m_p-1;\eta_v,\beta_v\rangle$$
$$=\langle\eta_u,\beta_u|\operatorname{Re}E_{pq}|\eta_v,\beta_v\rangle[(I-m_q+1)(I+m_q)]^{\frac{1}{2}}[(I-m_p+1)(I+m_p)]^{\frac{1}{2}}.\tag{120}$$

Thus, from Eqs. (119), (120), (117), (116), (114) and with $\epsilon_{[q]}(m_q)=-\hbar\gamma m_qH_{\text{ext}}\equiv-\hbar\omega_Lm_q$, we have

$$w_{[q]}{}^{\text{equil}}(m_q;m_q-1;t)=(I-m_q+1)(I+m_q)(2\pi/\hbar)\sum_{\eta_u,\beta_u,\eta_v,\beta_v}[\exp(-\eta_v/\Theta)/\sum_{\eta_w,\beta_w}\exp(-\eta_w/\Theta)]$$
$$\times\{\delta(\eta_u-\eta_v-\hbar\omega_L)[\sum_f|\langle\eta_u,\beta_u|C_{fq}|\eta_v,\beta_v\rangle|^2(\langle\langle m_f^2\rangle\rangle-(\langle\langle m_f\rangle\rangle)^2)$$
$$+|\langle\eta_u,\beta_u|\sum_fC_{fq}|\eta_v,\beta_v\rangle|^2(\langle\langle m_f\rangle\rangle)^2]+\delta(\eta_u-\eta_v-2\hbar\omega_L)$$
$$\times[\sum_f|\langle\eta_u,\beta_u|\operatorname{Re}E_{fq}|\eta_v,\beta_v\rangle|^2(I(I+1)-\langle\langle m_f^2\rangle\rangle+\langle\langle m_f\rangle\rangle)]\},\tag{121}$$

with

$$\langle\langle m_f\rangle\rangle\equiv\frac{\sum_{m_f}m_f\exp(\hbar\omega_Lm_f/\Theta)}{\sum_{m_f}\exp(\hbar\omega_Lm_f/\Theta)}\cong(\hbar\omega_L\Theta)\tfrac{1}{3}I(I+1),$$
$$\langle\langle m_f^2\rangle\rangle\equiv\frac{\sum_{m_f}m_f^2\exp(\hbar\omega_Lm_f/\Theta)}{\sum_{m_f}\exp(\hbar\omega_Lm_f/\Theta)}\cong\tfrac{1}{3}I(I+1),\tag{122}$$

whence, for H_{ext}, T such that $\hbar\omega_L/\Theta\ll1$,

$$w_{[q]}{}^{\text{equil}}(m_q;m_q-1;t)\cong(I-m_q+1)(I+m_q)\tfrac{1}{3}I(I+1)(2\pi/\hbar)\sum_{\eta_u,\beta_u,\eta_v,\beta_v}[\exp(-\eta_v/\Theta)/\sum_{\eta_w,\beta_w}\exp(-\eta_w/\Theta)]$$
$$\times\sum_f\{\delta(\eta_u-\eta_v-\hbar\omega_L)|\langle\eta_u,\beta_u|C_{fq}|\eta_v,\beta_v\rangle|^2+\delta(\eta_u-\eta_v-2\hbar\omega_L)2|\langle\eta_u,\beta_u|\operatorname{Re}E_{fq}|\eta_v,\beta_v\rangle|^2\}$$
$$\equiv(I-m_q+1)(I+m_q)w.\tag{123}$$

The shape dependent term, $|\langle\eta_u,\beta_u|\sum_fC_{fq}|\eta_v,\beta_i\rangle|^2(\langle\langle m_f\rangle\rangle)^2$, in Eq. (121) contains the factor

$$(\hbar\omega_L/\Theta)^2=(\hbar\gamma H_{\text{ext}}/kT)^2$$

[Eq. (122)] and so becomes important at extremely low temperatures.

In a similar way we can work out $w_{[q]}^{\text{equil}}(m_q-1;m_q;t)$ and obtain, consistent with Eqs. (116), (114), (115)

$$w_{[q]}^{\text{equil}}(m_q-1;m_q;t)=w_{[q]}^{\text{equil}}(m_q;m_q-1;t)\frac{\exp[-\epsilon_{[q]}(m_q-1)/\Theta]}{\exp[-\epsilon_{[q]}(m_q)/\Theta]}=w_{[q]}^{\text{equil}}(m_q;m_q-1;t)\exp(-\hbar\omega_L/\Theta). \quad (124)$$

An analogous discussion can be given for the case of the electric quadrupole spin-lattice interaction; here,

$$\begin{aligned}
\mathcal{V}_{\text{quad}}^{\text{nonsecular}}&=\sum_f[A_f(I_{[f]z}I_{[f]+}+I_{[f]+}I_{[f]z})+A_f'(I_{[f]+})^2]+\text{Herm. conj.}\\
A_f&\equiv[Q/8I(2I-1)](U_{[f];x,y}-U_{[f];y,z}),\\
A_f'&\equiv[Q/8I(2I-1)](U_{[f];x,x}-U_{[f];y,y}-2iU_{[f];x,y}),\\
U_{[f];x,x}&=\left.\frac{\partial^2U(\mathbf{r})}{\partial x\partial x}\right|_{\mathbf{r}=\mathbf{R}_f+\xi_f}\quad\text{etc.,}
\end{aligned}\quad (125)$$

where $Q\equiv$ nuclear quadrupole moment, and $U(\mathbf{r})\equiv$ lattice electrostatic potential at $\mathbf{r}$. A calculation similar to that in Eqs. (119)–(123), yields:

$$\begin{aligned}
w_{[q]}^{\text{equil}}(m_q;m_q-1;t)&=(2m_q-1)^2(I-m_q+1)(I+m_q)(2\pi/\hbar)\\
&\quad\times\sum_{\eta_u,\beta_u,\eta_v,\beta_v}\left(\frac{\exp(-\eta_v/\Theta)}{\sum_{\eta_w,\beta_w}\exp(-\eta_w/\Theta)}\right)\delta(\eta_u-\eta_v-\hbar\omega_L)|\langle\eta_u,\beta_u|A_q|\eta_v,\beta_v\rangle|^2\\
&\equiv(2m_q-1)^2(I-m_q+1)(I+m_q)w',
\end{aligned}\quad (126)$$

$$\begin{aligned}
w_{[q]}^{\text{equil}}(m_q;m_q-2;t)&=(I-m_q+2)(I-m_q+1)(I+m_q)(I+m_q-1)(2\pi/\hbar)\\
&\quad\times\sum_{\eta_u,\beta_u,\eta_v,\beta_v}\left(\frac{\exp(-\eta_v/\Theta)}{\sum_{\eta_w,\beta_w}\exp(-\eta_w/\Theta)}\right)\delta(\eta_u-\eta_v-2\hbar\omega_L)|\langle\eta_u,\beta_u|A_q'|\eta_v,\beta_v\rangle|^2\\
&\equiv(I-m_q+2)(I-m_q+1)(I+m_q)(I+m_q-1)w''.
\end{aligned}\quad (127)$$

Again, consistent with Eq. (116) or Eq. (115), we have:

$$\begin{aligned}
w_{[q]}^{\text{equil}}(m_q-1;m_q;t)&=w_{[q]}^{\text{equil}}(m_q;m_q-1;t)\frac{\exp[-\epsilon_{[q]}(m_q-1)/\Theta]}{\exp[-\epsilon_{[q]}(m_q)/\Theta]}\\
&=w_{[q]}^{\text{equil}}(m_q;m_q-1;t)\exp(-\hbar\omega_L/\Theta),
\end{aligned}\quad (128)$$

$$\begin{aligned}
w_{[q]}^{\text{equil}}(m_q-2;m_q;t)&=w_{[q]}^{\text{equil}}(m_q;m_q-2;t)\frac{\exp[-\epsilon_{[q]}(m_q-2)/\Theta]}{\exp[-\epsilon_{[q]}(m_q)/\Theta]}\\
&=w_{[q]}^{\text{equil}}(m_q;m_q-2;t)\exp[-2\hbar\omega_L/\Theta].
\end{aligned}\quad (129)$$

Having thus obtained the transition probabilities per unit time, $w_{[q]}^{\text{equil}}(m_q;m_q';t)$ [Eqs. (116), (121)–(124), (126)-(129)] we can use the methods of Section D to solve the individual particle "master" equation, Eqs. (110)–(115). Thus, on the basis of the analogous mathematical structure of Eqs. (110), (115) and Eqs. (75)–(80) we can apply the results of Eqs. (81)–(94), (104), (105) and write $(-I\leqq m_q\leqq I)$

$$\begin{aligned}
P_{[q]}(m_q;t)&=P_{[q]}^{\text{equil}}(m_q;t)+\sum_{\nu=1}^{2I}K_\nu(m_q)e^{-\omega_\nu(t-t_0)},\\
P_{[q]}^{\text{equil}}(m_q;t)&=\frac{\exp[-\epsilon_{[q]}(m_q)/\Theta]}{\sum_{m_q'}\exp[-\epsilon_{[q]}(m_q')/\Theta]}=\frac{\exp[\hbar\omega_Lm_q/\Theta]}{\sum_{m_q'}\exp[\hbar\omega_L\omega_q'/\Theta]},
\end{aligned}\quad (130)$$

where the ω_ν are eigenvalues of the matrix

$$-\|w_{[q]}{}^{\text{equil}}\| \equiv -\begin{vmatrix} -(1/T_I) & w_{[q]}{}^{\text{equil}}(I;I-1;t) & \cdots & w_{[q]}{}^{\text{equil}}(I;-I;t) \\ w_{[q]}{}^{\text{equil}}(I-1;I;t) & -(1/T_{I-1}) & \cdots & w_{[q]}{}^{\text{equil}}(I-1;-I;t) \\ \vdots & \vdots & & \vdots \\ w_{[q]}{}^{\text{equil}}(-I;I;t) & w_{[q]}{}^{\text{equil}}(-I;I-1;t) & \cdots & -(1/T_{-I}) \end{vmatrix}, \tag{131}$$

$$(1/T_I)=\sum_{m_q=I-1}^{-I} w_{[q]}{}^{\text{equil}}(m_q;I;t), \quad \text{etc.,}$$

and

$$K_\nu(m_q)=\left\{\left(\frac{dD(s)}{ds}\right)^{-1} C(m_q;s)\right\}_{s=-\omega_\nu};$$

$$D(s)\equiv\det(s\|1\|-\|w_{[q]}{}^{\text{equil}}\|); \tag{132}$$

$C(m_q;s)\equiv$ same determinant as $D(s)$ but with the column corresponding to m_q replaced by

$$\begin{vmatrix} P_{[q]}(I;t_0) \\ P_{[q]}(I-1;t_0) \\ \vdots \\ P_{[q]}(-I;t_0) \end{vmatrix}.$$

Thus the ω_ν and $K_\nu(m_q)$ are functionally determined by the $w_{[q]}{}^{\text{equil}}(m_q;m_q';t)$ and the $w_{[q]}{}^{\text{equil}}(m_q;m_q';t)$, $P_{[q]}(m_q';t_0)$, respectively. However, the explicit evaluation of the functions in question, apart from particularly simple cases [as in Eqs. (101)–(103)], is rather complicated.

Once the probability at time t of finding the spin $[q]$ in the state $\psi_{[q]}(m_q)$, $P_{[q]}(m_q;t)$, is known we can determine the longitudinal magnetization, $\langle\mu\rangle_t$, of the system of interest $[A]$ composed of the individual spins $[q]$. Thus $\langle\mu\rangle_t$ is given by:

$$\begin{aligned}\langle\mu\rangle_t&=\sum_{m_q=-I}^{I} P_{[q]}(m_q;t) \times\left\langle\psi_{[q]}(m_q)\left|\left(\frac{N_{[A]}}{V_{[A]}}\hbar\gamma\right)I_{[q]z}\right|\psi_{[q]}(m_q)\right\rangle \\ &=\sum_{m_q=-I}^{I} P_{[q]}(m_q;t)\left(\frac{N_{[A]}}{V_{[A]}}\hbar\gamma m_q\right),\end{aligned} \tag{133}$$

so that using Eq. (130), and in view of Eq. (122),

$$\begin{aligned}\langle\mu\rangle_t&=\left(\hbar\gamma\frac{N_{[A]}}{V_{[A]}}\right)\left\{\sum_{m_q=-I}^{I} P_{[q]}{}^{\text{equil}}(m_q;t)m_q +\sum_{\nu=1}^{2I}\left(\sum_{m_q=-I}^{I} K_\nu(m_q)m_q\right)e^{-\nu_\nu(t-t_0)}\right\} \\ &=\langle\mu\rangle_t{}^{\text{equil}}+\left(\hbar\gamma\frac{N_{[A]}}{V_{[A]}}\right) \times\sum_{\nu=1}^{2I}\left(\sum_{m_q=-I}^{I} K_\nu(m_q)m_q\right)e^{-\omega_\nu(t-t_0)};\end{aligned}$$

$$\begin{aligned}\langle\mu\rangle_t{}^{\text{equil}}&=\hbar\gamma\frac{N_{[A]}}{V_{[A]}}\langle\langle m_q\rangle\rangle\cong H_{\text{ext}}\frac{N_{[A]}}{V_{[A]}}\frac{\hbar^2\gamma^2}{\Theta}\tfrac{1}{3}I(I+1) \\ &=\frac{N_{[A]}}{V_{[A]}}\tfrac{1}{3}\hbar\gamma I(I+1)\left(\frac{\hbar\omega_L}{\Theta}\right).\end{aligned} \tag{134}$$

We now discuss the evaluation of the ω_ν, $K_\nu(m_q)$ in various special cases of interest in magnetic resonance.

Case I: $I=1$ with $\mathcal{V}_{\text{dip-dip}}\gg\mathcal{V}_{\text{quad}}$. Then from Eqs. (123), (124)

$$\begin{aligned}w_{[q]}{}^{\text{equil}}(1;0;t)&=1\cdot 2w=w_{[q]}{}^{\text{equil}}(0;1;t)\exp(\hbar\omega_L/\Theta) \\ &\cong w_{[q]}{}^{\text{equil}}(0;1;t)(1+\hbar\omega_L/\Theta), \\ w_{[q]}{}^{\text{equil}}(0,-1;t)&=2\cdot 1w \\ &=w_{[q]}{}^{\text{equil}}(-1;0;t)\exp(\hbar\omega_L/\Theta) \\ &\cong w_{[q]}{}^{\text{equil}}(-1;0;t)(1+\hbar\omega_L/\Theta), \\ w_{[q]}{}^{\text{equil}}(1;-1;t)&=w_{[q]}{}^{\text{equil}}(-1;1;t)=0.\end{aligned} \tag{135}$$

Equations (135), (131), (132), (134) yield

$$\begin{aligned}\omega_1&=(2-\hbar\omega_L/\Theta)w\cong 2w; \\ \omega_2&=(2-\hbar\omega_L/\Theta)3w\cong 6w;\end{aligned} \tag{136}$$

$$\begin{aligned}\frac{\langle\mu\rangle_t-\langle\mu\rangle_t{}^{\text{equil}}}{(\hbar\gamma N_{[A]}/V_{[A]})} &=-\tfrac{1}{4}e^{-2w(t-t_0)}\{(4+3\hbar\omega_L/\Theta)P_{[q]}(-1;t_0) \\ &\quad+(2\hbar\omega_L/\Theta)P_{[q]}(0;t_0)-(4-3\hbar\omega_L/\Theta)P_{[q]}(1;t_0)\} \\ &\quad-\tfrac{1}{12}e^{-6w(t-t_0)}(\hbar\omega_L/\Theta)\{-P_{[q]}(-1;t_0) \\ &\quad+2P_{[q]}(0;t_0)-P_{[q]}(1;0)\},\end{aligned} \tag{137}$$

so that, in general, the longitudinal magnetization $\langle\mu\rangle_t$ approaches its equilibrium value with two relaxation times, $(2w)^{-1}$, $(6w)^{-1}$. On the other hand, in magnetic resonance practice under the condition of initial saturation, we have the various $P_{[q]}(m_q;t_0)$ mutually equal so that $\langle\mu\rangle_{t0}=0$. With

$$P_{[q]}(1;t_0)=P_{[q]}(0;t_0)=P_{[q]}(-1;t_0)=\tfrac{1}{3},$$

Eq. (137) becomes

$$\begin{aligned}\frac{\langle\mu\rangle_t-\langle\mu\rangle_t{}^{\text{equil}}}{(\hbar\gamma N_{[A]}/V_{[A]})}&=-\tfrac{2}{3}(\hbar\omega_L/\Theta)e^{-2w(t-t_0)} \\ &=-\frac{\langle\mu\rangle_t{}^{\text{equil}}e^{-2w(t-t_0)}}{(\hbar\gamma N_{[A]}/V_{[A]})},\end{aligned} \tag{138}$$

so that in this case the longitudinal magnetization $\langle\mu\rangle_t$ approaches its equilibrium value $\langle\mu\rangle_t{}^{\text{equil}}$ with a single

relaxation time, $(2w)^{-1}$. Another interesting initial condition corresponds to $P_{[q]}(m_q;t_0)=\frac{1}{3}(1+\alpha m_q)$ with $|\alpha|\ll 1$; e.g., $\alpha=\hbar\omega_L/\Theta$ for $P_{[q]}(m_q;t_0)=P_{[q]}^{\text{equil}}(m_q;t)$, and $\alpha=-\hbar\omega_L/\Theta$ for $P_{[q]}(m_q;t_0)$ descriptive of the (negative temperature) situation "immediately after a sudden reversal of H_{ext}." Equation (137) now becomes

$$\frac{\langle\mu\rangle_t-\langle\mu\rangle_t^{\text{equil}}}{(\hbar\gamma N_{[A]}/V_{[A]})}=-\frac{2}{3}\left(\frac{\hbar\omega_L}{\Theta}-\alpha\right)e^{-2w(t-t_0)}$$
$$=-\frac{\langle\mu\rangle_t^{\text{equil}}[1-\alpha/(\hbar\omega_L/\Theta)]e^{-2w(t-t_0)}}{(\hbar\gamma N_{[A]}/V_{[A]})},\quad(139)$$

so that $\langle\mu\rangle_t$ again approaches $\langle\mu\rangle_t^{\text{equil}}$ with a single relaxation time. It is also interesting to note that

$$T(\text{min})=T_0=[w_{[q]}^{\text{equil}}(-1;0;t)+w_{[q]}^{\text{equil}}(1;0;t)]^{-1}\cong(4w)^{-1}<2(\omega_2)^{-1}=(3w)^{-1}$$

in agreement with Eq. (95), while

$$T(\text{max})=T_1=(w_{[q]}^{\text{equil}}(0;1;t))^{-1}\cong(2w)^{-1}\cong(\omega_1)^{-1}$$

in agreement with Eq. (100).

Case II: $I=\frac{3}{2}$ with $\mathcal{V}_{\text{dip-dip}}\gg\mathcal{V}_{\text{quad}}$. Then from Eqs. (123), (124),

$$\begin{aligned}
&w_{[q]}^{\text{equil}}(\tfrac{3}{2};\tfrac{1}{2};t)\\
&\quad=1\cdot 3w=w_{[q]}^{\text{equil}}(\tfrac{1}{2};\tfrac{3}{2};t)\exp(\hbar\omega_L/\Theta)\\
&\qquad\cong w_{[q]}^{\text{equil}}(\tfrac{1}{2},\tfrac{3}{2};t)(1+\hbar\omega_L/\Theta),\\
&w_{[q]}^{\text{equil}}(\tfrac{1}{2};-\tfrac{1}{2};t)\\
&\quad=2\cdot 2w=w_{[q]}^{\text{equil}}(-\tfrac{1}{2};\tfrac{1}{2};t)\exp(\hbar\omega_L/\Theta)\\
&\qquad\cong w_{[q]}^{\text{equil}}(-\tfrac{1}{2};\tfrac{1}{2};t)(1+\hbar\omega_L/\Theta),\quad(140)\\
&w_{[q]}^{\text{equil}}(-\tfrac{1}{2},-\tfrac{3}{2};t)\\
&\quad=3\cdot 1w=w_{[q]}^{\text{equil}}(-\tfrac{3}{2};-\tfrac{1}{2};t)\exp(\hbar\omega_L/\Theta)\\
&\qquad\cong w_{[q]}^{\text{equil}}(-\tfrac{3}{2};-\tfrac{1}{2};t)(1+\hbar\omega_L/\Theta),\\
&w_{[q]}^{\text{equil}}(\tfrac{3}{2};-\tfrac{1}{2};t)\\
&\quad=w_{[q]}^{\text{equil}}(-\tfrac{1}{2};\tfrac{3}{2};t)=w_{[q]}^{\text{equil}}(\tfrac{3}{2};-\tfrac{3}{2};t)\\
&\qquad=w_{[q]}^{\text{equil}}(-\tfrac{3}{2};\tfrac{3}{2};t)=0,
\end{aligned}$$

so that from Eqs. (131)–(134) and under the condition of initial saturation

$$\begin{aligned}
\omega_1&=(2-\hbar\omega_L/\Theta)\cong 2w;\\
\omega_2&=(2-\hbar\omega_L/\Theta)3w\cong 6w;\qquad(141)\\
\omega_3&=(2-\hbar\omega_L/\Theta)6w\cong 12w;
\end{aligned}$$

$$\frac{\langle\mu\rangle_t-\langle\mu_t\rangle^{\text{equil}}}{(\hbar\gamma N_{[A]}/V_{[A]})}=-\frac{5}{4}\frac{\hbar\omega_L}{\Theta}e^{-2w(t-t_0)}$$
$$=-\frac{\langle\mu\rangle_t^{\text{equil}}e^{-2w(t-t_0)}}{(\hbar\gamma N_{[A]}/V_{[A]})}.\quad(142)$$

Thus the longitudinal magnetization $\langle\mu\rangle_t$ again approaches its equilibrium value $\langle\mu\rangle_t^{\text{equil}}$ with a single relaxation time, $(2w)^{-1}$.

Case III: $I=1$ with $\mathcal{V}_{\text{quad}}\gg\mathcal{V}_{\text{dip-dip}}$. Then from Eqs. (126)–(129),

$$\begin{aligned}
&w_{[q]}^{\text{equil}}(1;0;t)\\
&\quad=1\cdot 1\cdot 2w'=w_{[q]}^{\text{equil}}(0;1;t)\exp(\hbar\omega_L/\Theta)\\
&\qquad\cong w_{[q]}^{\text{equil}}(0;1;t)(1+\hbar\omega_L/\Theta),\\
&w_{[q]}^{\text{equil}}(0;-1;t)\\
&\quad=1\cdot 2\cdot 1w'=w_{[q]}^{\text{equil}}(-1;0;t)\exp(\hbar\omega_L/\Theta)\\
&\qquad\cong w_{[q]}^{\text{equil}}(-1;0;t)(1+\hbar\omega_L/\Theta),\quad(143)\\
&w_{[q]}^{\text{equil}}(1;-1;t)\\
&\quad=2\cdot 1\cdot 2\cdot 1w''=w_{[q]}^{\text{equil}}(-1;1;t)\exp(2\hbar\omega_L/\Theta)\\
&\qquad\cong w_{[q]}^{\text{equil}}(-1;1;t)(1+2\hbar\omega_L/\Theta),
\end{aligned}$$

so that from Eqs. (131)–(134) and under the condition of initial saturation,

$$\omega_1=(2-\hbar\omega_L/\Theta)w'+(2-2\hbar\omega_L/\Theta)4w''\cong 2w'+8w'',\quad(144)$$

$$\omega_2=(2-\hbar\omega_L/\Theta)2w'\cong 6w',$$

$$\begin{aligned}
\frac{\langle\mu\rangle_t-\langle\mu\rangle_t^{\text{equil}}}{(\hbar\gamma N_{[A]}/V_{[A]})}&=-\frac{2}{3}\left(\frac{\hbar\omega_L}{\Theta}\right)e^{-(2w'+8w'')(t-t_0)}\\
&=-\frac{\langle\mu\rangle_t^{\text{equil}}e^{-(2w'+8w'')(t-t_0)}}{(\hbar\gamma N_{[A]}/V_{[A]})},
\end{aligned}\quad(145)$$

whence $\langle\mu\rangle_t$ once more approaches $\langle\mu\rangle_t^{\text{equil}}$ with a single relaxation time, $(2w'+8w'')^{-1}$.

The evolution in time of $\langle\mu\rangle_t$ toward $\langle\mu\rangle_t^{\text{equil}}$ [as in Eqs. (137)–(139), (142), (145)] has also been treated in terms of the concept of a time-dependent "spin-temperature" $T_s(t)$. For a comparison of the results obtained here with the not always correct results deduced by means of the spin-temperature procedure, see Appendix C.

G. MAGNETIC RESONANCE: TIME VARIATION OF TRANSVERSE MAGNETIZATION

We shall now analyze the variation in time of $\langle\mu'\rangle_t$, the transverse magnetization of the system of interest $[A]$ composed of the individual spins $[q]$. We have:

$$\langle\mu'\rangle_t=\left\langle(\hbar\gamma/V_{[A]})\sum_{q=1}^{N[A]}I_{[q]x}\right\rangle_t\equiv\langle(\hbar\gamma/V_{[A]})I_x\rangle_t.\quad(146)$$

Such a nonvanishing transverse magnetization may be obtained at the initial time t_0 by the application of a (very short) "90°" rf pulse at a carrier frequency equal to $\omega_L=\gamma H_{\text{ext}}$ which rotates the previously existing equilibrium longitudinal magnetization into the plane perpendicular to $\mathbf{H}_{\text{ext}}=H_{\text{ext}}\hat{z}$; thus immediately after

the pulse, we have in view of Eqs. (2), (4), (5), (50), (51),

$$\begin{aligned}\rho(t_0)&=\exp[i(\pi/2)(-I_y)]\rho^{\text{equil}}\exp[-i(\pi/2)(-I_y)]\\&=\exp[-i(\pi/2)I_y]\left(\frac{\exp(-\mathcal{H}_{[A]}{}^{(0)}/\Theta)\exp(-\mathcal{H}_{[B]}{}^{(0)}/\Theta)}{\text{Trace}[\exp(-\mathcal{H}_{[A]}{}^{(0)}/\Theta)\exp(-\mathcal{H}_{[B]}{}^{(0)}/\Theta)]}\right)\exp[i(\pi/2)I_y]\\&=\exp[-i(\pi/2)I_y]\left(\frac{\exp(\hbar\omega_L I_z/\Theta)\exp(-\mathcal{H}_{[B]}{}^{(0)}/\Theta)}{\text{Trace}[\exp(\hbar\omega_L I_z/\Theta)\exp(-\mathcal{H}_{[B]}{}^{(0)}/\Theta)]}\right)\exp[i(\pi/2)I_y]\\&=\frac{\exp(\hbar\omega_L I_x/\Theta)\exp(-\mathcal{H}_{[B]}{}^{(0)}/\Theta)}{\mathfrak{N}\exp(-E/\Theta)};\quad E\equiv E_m{}^{(0)}\cong E_n{}^{(0)}\cong\cdots,\end{aligned}\tag{147}$$

$$\begin{aligned}\langle\mu'\rangle_{t_0}&=\text{Trace}\{\rho(t_0)\mu'\}=(\hbar\gamma/V_{[A]})\,\text{Trace}\{\rho(t_0)I_x\}\\&=\frac{\hbar\gamma}{V_{[A]}}\frac{\text{Trace}\{\exp(\hbar\omega_L I_x/\Theta)I_x\}}{\text{Trace}\{\exp(\hbar\omega_L I_x/\Theta)\}}=\langle\mu\rangle_t{}^{\text{equil}}\\&\cong(N_{[A]}/V_{[A]})\tfrac{1}{3}\hbar\gamma I(I+1)\hbar\omega_L/\Theta.\end{aligned}\tag{148}$$

The description of the variation of $\langle\mu'\rangle_t$ with $t(t>t_0)$ is most easily given in a frame of reference "rotating with angular velocity $\omega_L\hat{z}$ relative to the laboratory frame" and we proceed to generalize our discussion to the treatment of phenomena in such "rotating" frames.

We begin with Eq. (5) for $\langle\mu'\rangle_t$, viz.,

$$\langle\mu'\rangle_t=\text{Trace}\{\rho(t)\mu'\}=\text{Trace}\{\rho_{\text{rot}}(t)\mu_{\text{rot}}'(t)\},\tag{149}$$

where

$$\rho_{\text{rot}}(t)\equiv e^{-i\omega_L(t-t_0)I_z}\rho(t)e^{i\omega_L(t-t_0)I_z},\tag{150}$$

$$\mu_{\text{rot}}'(t)\equiv e^{-i\omega_L(t-t_0)I_z}\mu'e^{i\omega_L(t-t_0)I_z},\tag{151}$$

the subscript rot indicating operators in the "rotating" frame. Use of Eq. (2) with $\mathcal{H}\equiv\mathcal{H}_{[A]}{}^{(0)}+\mathcal{H}_{[B]}{}^{(0)}+\mathcal{V}=-\hbar\omega_L I_z+\mathcal{H}_{[B]}{}^{(0)}+\mathcal{V}$ and of Eq. (146) in Eqs. (150), (151) yields,

$$\begin{aligned}\rho_{\text{rot}}(t)=e^{-i\omega_L(t-t_0)I_z}\{&\exp[i\omega_L(t-t_0)I_z\\&-(i/\hbar)(t-t_0)(\mathcal{H}_{[B]}{}^{(0)}+\mathcal{V})]\rho(t_0)\\&\times\exp[-i\omega_L(t-t_0)I_z+(i/\hbar)(t-t_0)\\&\times(\mathcal{H}_{[B]}{}^{(0)}+\mathcal{V})]\}e^{i\omega_L(t-t_0)}I_z,\end{aligned}\tag{152}$$

$$\begin{aligned}\mu_{\text{rot}}'(t)=(\hbar\gamma/V_{[A]})\{&I_x\cos[\omega_L(t-t_0)]\\&+I_y\sin[\omega_L(t-t_0)]\},\end{aligned}\tag{153}$$

so that, substituting Eq. (153) into Eq. (149),

$$\begin{aligned}\langle\mu'\rangle_t=(\hbar\gamma/V_{[A]})(&\cos[\omega_L(t-t_0)]\,\text{Trace}\{\rho_{\text{rot}}(t)I_x\}\\&+\sin[\omega_L(t-t_0)]\,\text{Trace}\{\rho_{\text{rot}}(t)I_y\}),\end{aligned}\tag{154}$$

with $\rho_{\text{rot}}(t)$ given by Eq. (152), and $\rho_{\text{rot}}(t_0)=\rho(t_0)$ by Eq. (147).

The expression for $\rho_{\text{rot}}(t)$ in Eq. (152) is considerably simplified if,

$$[\mathcal{H}_{[A]}{}^{(0)},\mathcal{V}]=0,\tag{155}$$

i.e.,

$$[I_z,\mathcal{V}]=0\tag{156}$$

the Eqs. (156), (152) yielding,

$$\begin{aligned}\rho_{\text{rot}}(t)=\exp[-(i/\hbar)(t-t_0)(\mathcal{H}_{[B]}{}^{(0)}+\mathcal{V})]\rho(t_0)\\\times\exp[(i/\hbar)(t-t_0)(\mathcal{H}_{[B]}{}^{(0)}+\mathcal{V})].\end{aligned}\tag{157}$$

If in addition,

$$[\mathcal{H}_{[B]}{}^{(0)},\mathcal{V}]=0,\tag{158}$$

the Eqs. (157) and (147) give

$$\begin{aligned}\rho_{\text{rot}}(t)=\exp[-(i/\hbar)(t-t_0)\mathcal{V}]\rho(t_0)\\\times\exp[(i/\hbar)(t-t_0)\mathcal{V}].\end{aligned}\tag{159}$$

It is further reasonable to suppose on physical grounds that $\text{Trace}\{\rho_{\text{rot}}I_y\}=0$ for ρ_{rot} given either by Eq. (157) or (159) so that

$$\begin{aligned}\langle\mu'\rangle_t=(\hbar\gamma/V_{[A]})(&\cos[\omega_L(t-t_0)]\\&\times\text{Trace}\{\rho_{\text{rot}}(t)I_x\}).\end{aligned}\tag{160}$$

Equation (160) corresponds to the assumption that, in the frame of reference rotating with angular velocity $\omega_L\hat{z}$ relative to the laboratory frame, $\langle\mu'\rangle_t$ approaches $\langle\mu'\rangle_t{}^{\text{equil}}$ without any further precession.[15]

Equation (160) shows that the problem of evaluating $\langle\mu'\rangle_t$ is reduced to the problem of evaluating

$$\text{Trace}\{\rho_{\text{rot}}(t)I_x\}$$

which can be written, using Eqs. (5), (6), as

$$\begin{aligned}\text{Trace}\{\rho_{\text{rot}}(t)I_x\}&=\textstyle\sum_n\langle\phi_n|\rho_{\text{rot}}(t)|\phi_n\rangle\langle\phi_n|I_x|\phi_n\rangle\\&=\textstyle\sum_n P_{\text{rot}}(n;t)\langle\phi_n|I_x|\phi_n\rangle,\end{aligned}\tag{161}$$

provided that the matrix of I_x is diagonal with respect to the complete set of states ϕ_n. The quantity $P_{\text{rot}}(n;t)=\langle\phi_n|\rho_{\text{rot}}(t)|\phi_n\rangle$ is the probability that $[A+B]$ is found at time t in the state ϕ_n. Equations (160), (161) for

[15] See I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957), who have also demonstrated by an explicit but approximate calculation in the case $I=\frac{1}{2}$ that Trace $\{\rho_{\text{rot}}I_y\}=0$ for ρ_{rot} given by Eq. (159) with $\mathcal{V}=\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}$ as in Eq. (168) below.

$\langle\mu'\rangle_t$ are analogous to Eq. (133) for $\langle\mu\rangle_t$ and may be evaluated in the same way if the $P_{\mathrm{rot}}(n;t)$ satisfy an equation of the "master" type.

We now discuss whether $P_{\mathrm{rot}}(n;t)=\langle\phi_n|\rho_{\mathrm{rot}}(t)|\phi_n\rangle$ satisfies a "master" equation analogous to that satisfied by the $P(n;t)$ of Eq. (35). First of all, we note that if the ϕ_n are such that $\langle\phi_m|I_x|\phi_n\rangle=\langle\phi_n|I_x|\phi_n\rangle\delta_{mn}$, i.e., $I_x=\{I_x\}^{\mathrm{diag}}$, then for the $\rho(t_0)=\rho_{\mathrm{rot}}(t_0)$ of Eqs. (147) and (152):

$$\begin{aligned}\langle\phi_m|\rho_{\mathrm{rot}}(t_0)|\phi_n\rangle&=\langle\phi_n|\rho_{\mathrm{rot}}(t_0)|\phi_n\rangle\delta_{mn}\\&=P_{\mathrm{rot}}(n;t_0)\delta_{mn},\text{ i.e., }\rho_{\mathrm{rot}}(t_0)=\{\rho_{\mathrm{rot}}(t_0)\}^{\mathrm{diag}}.\end{aligned}$$

Then, following the procedures of Eqs. (7)–(11) and Eqs. (13)–(16), the Eqs. (157) and (159) yield the analogs of Eqs. (11), (8), (9), and (14) and Eq. (16), viz.,

$$\begin{aligned}\frac{P_{\mathrm{rot}}(n;t+\tau)-P_{\mathrm{rot}}(n;t)}{\tau}&=\sum_m\left[W_{\mathrm{rot};n,m}(\tau)P_{\mathrm{rot}}(m;t)-W_{\mathrm{rot};m,n}(\tau)P_{\mathrm{rot}}(n;t)\right]\\&\quad+Y_{\mathrm{rot};n}(\tau;t-t_0),\qquad(162)\end{aligned}$$

where

$$\begin{aligned}W_{\mathrm{rot};n,m}(\tau)&\\\equiv(1/\tau)&|\langle\phi_n|\exp[-(i/\hbar)\tau\mathcal{K}]|\phi_m\rangle|^2,\qquad(163)\end{aligned}$$

$$\begin{aligned}Y_{\mathrm{rot};n}(\tau;t-t_0)&\\\equiv(1/\tau)&\sum_{k,m}(1-\delta_{km})\langle\phi_n|\exp[-(i/\hbar)\tau\mathcal{K}]|\phi_m\rangle\\&\times\langle\phi_n|\exp[-(i/\hbar)\tau\mathcal{K}]|\phi_k\rangle^*\langle\phi_m|\rho_{\mathrm{rot}}(t)|\phi_k\rangle\\=(1/\tau)&\sum_{k,m,l}(1-\delta_{km})\langle\phi_n|\exp[-(i/\hbar)\tau\mathcal{K}]|\phi_m\rangle\qquad(164)\\&\times\langle\phi_n|\exp[-(i/\hbar)\tau\mathcal{K}]|\phi_k\rangle^*\\&\times\langle\phi_m|\exp[-(i/\hbar)(t-t_0)\mathcal{K}]|\phi_l]\\&\times\langle\phi_k|\exp[-(i/\hbar)(t-t_0)\mathcal{K}]|\phi_l\rangle^*P_{\mathrm{rot}}(l;t_0),\end{aligned}$$

with

$$\mathcal{K}\equiv\mathcal{H}_{[B]}^{(0)}+\mathcal{V}:\quad\rho_{\mathrm{rot}}(t)\quad\text{of Eq. (157)},\qquad(165)$$

$$\mathcal{K}\equiv\mathcal{V}:\quad\rho_{\mathrm{rot}}(t)\quad\text{of Eq. (159)},\qquad(166)$$

and

$$\begin{aligned}\frac{P_{\mathrm{rot}}(n;t)-P_{\mathrm{rot}}(n;t_0)}{t-t_0}&=\sum_m\left[W_{\mathrm{rot};n,m}(t-t_0)P_{\mathrm{rot}}(m;t_0)\right.\\&\quad\left.-W_{\mathrm{rot};m,n}(t-t_0)P_{\mathrm{rot}}(n;t_0)\right].\qquad(167)\end{aligned}$$

It remains, in order to demonstrate the equivalence of Eqs. (162)–(166) to a "master" equation, to show that the transition probability per unit time, $W_{\mathrm{rot};n;m}(\tau)$, is independent of τ for $\hbar/\xi_n\ll\tau\leqq t-t_0$ with ξ_n a suitably defined excitation energy per particle [analogous to the discussion in Eqs. (18), (19), (22)–(25); restrictions (*b*), (*c*) after Eq. (35)] and that $Y_{\mathrm{rot};n}(\tau;t-t_0)$ is relatively negligible [analogous to the discussion in Eqs. (27)–(34); restriction (*d*) after Eq. (35)].

To consider the questions raised in the preceding paragraph we distinguish two cases: (I) "Rigid" lattice; (II) "Nonrigid" lattice, and discuss them in order.

Case (I): "Rigid" Lattice

Here we suppose that

$$\mathcal{V}=\mathcal{V}(\cdots(\mathbf{R}_f+\xi_f)-(\mathbf{R}_g+\xi_g)\cdots;\cdots,\mathbf{I}_{[f]},\mathbf{I}_{[g]},\cdots)$$

is well approximated by

$$\mathcal{V}(\cdots(\mathbf{R}_f-\mathbf{R}_g)\cdots;\cdots,\mathbf{I}_{[f]},\mathbf{I}_{[g]},\cdots)$$

where $\mathcal{V}$ is the spin-lattice phonon interaction, e.g.,

$$\mathcal{V}=\mathcal{V}_{\mathrm{dip\text{-}dip}}=\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}+\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{nonsecular}},$$

with $\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{nonsecular}}$ given in Eq. (118) and

$$\begin{aligned}\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}=\tfrac{1}{2}\sum_{f,g}A_{fg}(I_{[f]x}I_{[g]x}&+I_{[f]y}I_{[g]y}\\&-2I_{[f]z}I_{[g]z}),\qquad(168)\end{aligned}$$

$$A_{fg}(\mathbf{r}_f-\mathbf{r}_g)\equiv-\tfrac{1}{2}(\hbar^2\gamma^2/r_{fg}^3)(1-3\cos^2\theta_{fg});$$

$$\mathbf{r}_f-\mathbf{r}_g\equiv(r_{fg},\theta_{fg},\phi_{fg}).$$

$\mathbf{r}_f=\mathbf{R}_f+\xi_f$; $\mathbf{R}_f\equiv$lattice vector of the atom $[f]$; $\xi_f\equiv$displacement of the atom $[f]$ from its lattice position=function of phonon creation and destruction operators.

The neglect within $\mathcal{V}$ of ξ_f, ξ_g compared to $\mathbf{R}_f$, $\mathbf{R}_g$ corresponds to the physical assumption of the "rigid" lattice and to the neglect of any energy interchanges between the spins and the lattice; since $\mathcal{H}_{[B]}^{(0)}=\mathcal{H}_{[B]}^{(0)}(\cdots,\xi_f,\xi_g,\cdots)$ this neglect ensures that $[\mathcal{H}_{[B]}^{(0)},\mathcal{V}]=0$ [Eq. (158)] and implies the validity of Eq. (159) for $\rho_{\mathrm{rot}}(t)$ provided that in addition $[\mathcal{H}_{[A]}^{(0)},\mathcal{V}]=0$ [Eq. (155)]. This last commutator vanishes however if $\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{nonsecular}}$ is neglected compared to $\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}$, i.e., if

$$\begin{aligned}\mathcal{V}=\mathcal{V}_{\mathrm{dip\text{-}dip}}=\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}&+\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{nonsecular}}\\&\approx\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}},\qquad(169)\end{aligned}$$

an approximation valid in the "rigid" solid where energy interchanges between the spins and the lattice, associated with $\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{nonsecular}}$, are entirely unimportant.

We proceed to investigate the properties of $W_{\mathrm{rot};n,m}(\tau)$, $Y_{\mathrm{rot};n}(\tau;t-t_0)$ [Eqs. (163), (164), (166)] with

$$\begin{aligned}\mathcal{K}\equiv\mathcal{V}\approx\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}(\cdots,\mathbf{R}_f-\mathbf{R}_g,\cdots;&\\\cdots,\mathbf{I}_{[f]},\mathbf{I}_{[g]}\cdots),&\qquad(170)\end{aligned}$$

and, in accordance with the general method employed to deduce Eq. (25) from Eqs. (8), (10), decompose $\mathcal{K}$ as [see Eqs. (170), (168)]

$$\mathcal{K}=\mathcal{K}^{(0)}+\mathcal{U},$$

$$\mathcal{K}^{(0)}\equiv\tfrac{1}{2}\sum_{f,g}A_{fg}(\mathbf{R}_f-\mathbf{R}_g)(I_{[f]x}I_{[g]x}),\qquad(171)$$

$$\mathcal{U}\equiv\tfrac{1}{2}\sum_{f,g}A_{fg}(\mathbf{R}_f-\mathbf{R}_g)(I_{[f]y}I_{[g]y}-2I_{[f]z}I_{[g]z}),$$

and take for the ϕ_n

$$\phi_n=\{\phi_{[1]}(\mu_1)\phi_{[2]}(\mu_2)\cdots\phi_{[q]}(\mu_q)\cdots\}_{[A]}\psi_{[B]}(\eta_u,\beta_u),\quad(172)$$
$$I_{[q]x}\phi_{[q]}(\mu_q)=\mu_q\phi_{[q]}(\mu_q),$$
$$I_x\phi_n=\left(\sum_{q=1}^{N[A]}\mu_q\right)\phi_n,$$

whence

$$\mathcal{K}^{(0)}\phi_n=\mathcal{K}_n^{(0)}\phi_n=\tfrac{1}{2}\sum_{f,g}A_{fg}(\mathbf{R}_f-\mathbf{R}_g)\mu_f\mu_g \approx N_{[A]}(\hbar^2\gamma^2/a^3)\cong N_{[A]}\xi_n \quad (173)$$
$$(a\equiv\text{lattice spacing}).$$

We then have [see Eqs. (23)–(25)]

$$T_{\mathrm{rot};n}=[\sum_m W_{\mathrm{rot};m,n}(\tau)(1-\delta_{mn})]^{-1}$$
$$\approx[\sum_m(2\pi/\hbar)\delta(\mathcal{K}_m^{(0)}-\mathcal{K}_n^{(0)}) \times|\langle\phi_m|\mathfrak{U}|\phi_n\rangle|^2(1-\delta_{mn}]^{-1}\quad(174))$$
$$\approx\left[\frac{1}{\hbar}\frac{1}{(\hbar^2\gamma^2/a^3)}\left(\frac{\hbar^2\gamma^2}{a^3}\right)^2\right]^{-1}\approx\frac{\hbar}{\xi_n},$$

so that restriction (c), after Eq. (35), i.e., the analog of Eq. (24), is not satisfied and the quantity

$$W_{\mathrm{rot};n,m}(\tau)=(1/\tau)|\langle\phi_n|\exp[-(i/\hbar)\times\tau\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}(\cdots,\mathbf{R}_f-\mathbf{R}_g,\cdots;\cdots,\mathbf{I}_{[f]},\times\mathbf{I}_{[g]},\cdots)]|\phi_m\rangle|^2$$

of Eq. (163) is *not ever* effectively independent of τ. In addition $\mathfrak{U}\approx\mathcal{K}^{(0)}$ so that restriction (d) after Eq. (35), i.e., the analogs of Eqs. (29)–(34), is not satisfied either, and the term $Y_{\mathrm{rot};n}(\tau;t-t_0)$ of Eq. (164) (with $\mathcal{K}=\mathcal{V}\approx\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}(\cdots,\mathbf{R}_f-\mathbf{R}_g,\cdots;\cdots,\mathbf{I}_{[f]},\mathbf{I}_{[g]}\cdots)$, is *not* relatively negligible in Eq. (162) compared to the term

$$\sum_m[W_{\mathrm{rot};n,m}(\tau)P_{\mathrm{rot}}(m;t)-W_{\mathrm{rot};m,n}(\tau)P_{\mathrm{rot}}(n;t)].$$

Thus no "master" equation analogous to that of Eq. (35) for the $P(n;t)$ is satisfied by the $P_{\mathrm{rot}}(n;t)$ of Eq. (162) in the "rigid" lattice case and the correct determination of $P_{\mathrm{rot}}(n;t)$, $\langle\mu'\rangle_t$ must be made from the complete Eqs. (162)–(164) or from Eq. (167), together with Eqs. (161), (160), or alternatively, from Eqs. (159), (160). Such a correct determination of $\langle\mu'\rangle_t$ on the basis of Eqs. (159), (160):

$$\langle\mu'\rangle_t=(\hbar\gamma/V_{[A]})(\cos[\omega_L(t-t_0)]\times\mathrm{Trace}\{\exp[-(i/\hbar)(t-t_0)\mathcal{V}]\rho(t_0)\times\exp[(i/\hbar)(t-t_0)\mathcal{V}]I_x\}),\quad(175)$$

$$\mathcal{V}\approx\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}(\cdots,\mathbf{R}_f-\mathbf{R}_g,\cdots;\cdots,\mathbf{I}_{[f]},\mathbf{I}_{[g]}\cdots),$$

as in Eq. (168), $\rho(t_0)$ as in Eq. (147), has been given by Lowe and Norberg[15] and predicts a type of oscillatory approach to equilibrium for $\{\langle\mu'\rangle_t/\cos[\omega_L(t-t_0)]\}$—the Lowe-Norberg beats—which is observed (six beats are detected in CaF at 1.2°K!) and which can *never* be predicted by a calculation based on a "master" equation [see discussion at end of Sec. B and after Eq. (88)]. The Lowe-Norberg beats demonstrate in a dramatic fashion for the case of the "rigid" lattice the quantal coherence effects contained in the τ dependence of the term $W_{\mathrm{rot};n;m}(\tau)$ and in the presence of the term $Y_{\mathrm{rot};n}(\tau;t-t_0)$ in the complete Eqs. (162)–(164).

In summarizing the "rigid" lattice situation it must be emphasized that the "master" equation is inapplicable and that the quantal coherence effects are crucial because the physical coupling between the spins $[A]$ and the lattice $[B]$, i.e., the dependence of $\mathcal{V}$ on ξ_f, ξ_g is considered negligible [Eqs. (158), (159), (170), (169), (168) with $\mathbf{r}_f\cong\mathbf{R}_f$]. The supersystem $[A+B]$ is then decomposable into two effectively noninteracting parts: the set of coupled spins $[A^*]$ described by the Hamiltonian $\mathcal{H}_{[A]}^{(0)}+\mathcal{V}$ and the lattice $[B]$ described by the Hamiltonian $\mathcal{H}_{[B]}^{(0)}$, $([\mathcal{H}_{[A]}^{(0)}+\mathcal{V},\mathcal{H}_{[B]}^{(0)}]=0)$, the variation of $\langle\mu'\rangle_t$ with t referring in fact to phenomena occurring wholly within $[A^*]$.

Case (II): "Nonrigid" Lattice

To treat the case of the "nonrigid" lattice we begin with the always applicable Eqs. (162)–(164) with $\mathcal{K}$ given by Eq. (165), (169), (168),

$$\mathcal{K}=\mathcal{H}_{[B]}^{(0)}+\mathcal{V}\approx\mathcal{H}_{[B]}^{(0)}(\cdots\xi_f,\xi_g,\cdots)+\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}(\cdots,(\mathbf{R}_f+\xi_f)-(\mathbf{R}_g+\xi_g),\cdots;\cdots\mathbf{I}_{[f]},\mathbf{I}_{[g]},\cdots).\quad(176)$$

Thus the dependence of $\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}$ on the ξ_f is included but energy interchanges between the spins and the lattice are still considered relatively unimportant so that $\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{nonsecular}}$ is neglected compared to $\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}$, ensuring the validity of Eq. (155). Physically Case (I) applies for $T\ll T_{\mathrm{Debye}}$ and Case (II) for $T\gtrsim T_{\mathrm{Debye}}$.

We proceed to show that in this "nonrigid" lattice case Eqs. (162)–(165), (176) for $P_{\mathrm{rot}}(n;t)$ are well approximated by a "master" equation of the type of Eqs. (35), (36) for $P(n;t)$, viz.,

$$\frac{d}{dt}P_{\mathrm{rot}}(n;t)=\sum_m[W_{\mathrm{rot};n,m}P_{\mathrm{rot}}(m;t)-W_{\mathrm{rot};m,n}P_{\mathrm{rot}}(n;t)],\quad(177)$$

with time-independent transition probabilities per unit time

$$W_{\mathrm{rot};n,m}=(2\pi/\hbar)\delta(\eta_u-\eta_v)|\langle\phi_n|\mathcal{V}_{\mathrm{dip\text{-}dip}}^{\mathrm{secular}}|\phi_m\rangle|^2=W_{\mathrm{rot};m,n},\quad(178)$$

where

$$\phi_n=\phi_{[A]}(\{\mu_i\})\psi_{[B]}(\eta_u,\beta_u)\equiv\{\phi_{[1]}(\mu_1)\phi_{[2]}(\mu_2)\cdots\phi_{[i]}(\mu_i)\cdots\times\phi_{[q]}(\mu_q)\cdots\}_{[A]}\psi_{[B]}(\eta_u,\beta_u),$$
$$\phi_m=\phi_{[A]}(\{\mu_i'\})\psi_{[B]}(\eta_v,\beta_v)\equiv\{\phi_{[1]}(\mu_1')\phi_{[2]}(\mu_2')\cdots\phi_{[i]}(\mu_i')\cdots\times\phi_{[q]}(\mu_q')\cdots\}_{[A]}\psi_{[B]}(\eta_v,\beta_v),$$
$$\mathcal{H}_{[B]}^{(0)}\phi_n=\eta_u\phi_n;\quad\mathcal{H}_{[B]}^{(0)}\phi_m=\eta_v\phi_m,$$
$$I_{[q]x}\phi_{[q]}(\mu_q)=\mu_q\phi_{[q]}(\mu_q),\quad(179)$$
$$I_x\phi_n=\left(\sum_{q=1}^{N[A]}\mu_q\right)\phi_n.$$

The derivation of Eqs. (177), (178) from Eqs. (162)–(165), (176) is effected by essentially the same procedure as that used in Sec. B to obtain Eqs. (35), (36) from Eqs. (11), (8), (14) with $\mathcal{H}_{[B]}^{(0)}$ playing the role of $\mathcal{H}_{[A]}^{(0)}+\mathcal{H}_{[B]}^{(0)}\equiv\mathcal{H}^{(0)}$ and $\mathcal{V}_{\text{dip-dip}}^{\text{secular}}$ playing the role of $\mathcal{V}$. In particular, the validity of Eqs. (177), (178) follows from the validity, in this Case (II), of restrictions analogous to (*c*), (*d*) after Eq. (35), viz.,

$$\hbar/\xi_n\approx\hbar/kT_{\text{Debye}}\ll T_n=\Big[\sum_m W_{\text{rot};m,n}(1-\delta_{mn})\Big]^{-1}=\Big[\sum_m(2\pi/\hbar)\delta(\eta_v-\eta_u)\,|\langle\phi_m|\mathcal{V}_{\text{dip-dip}}^{\text{secular}}|\phi_n\rangle|^2(1-\delta_{mn})\Big]^{-1}$$
$$\approx\left[\frac{1}{\hbar}\left(\frac{1}{kT_{\text{Debye}}}\right)\left\langle\left(\frac{\hbar^2\gamma^2}{[(\mathbf{R}_f+\xi_f)-(\mathbf{R}_{f+1}+\xi_{f+1})]^3}\right)^2\right\rangle_{\text{av over }\xi}\right]^{-1}$$
$$\cong\left[\frac{1}{\hbar}\left(\frac{1}{kT_{\text{Debye}}}\right)\left(\frac{\hbar^2\gamma^2}{a^3}\right)^2\right]^{-1}, \tag{180}$$

and

$$\mathcal{V}_{\text{dip-dip}}^{\text{secular}}\ll\mathcal{H}_{[B]}^{(0)}, \tag{181}$$

while restriction (*a*) is ensured by the diagonal character, with respect to the $\mathcal{H}_{[B]}^{(0)}$ eigenstates ϕ_n of Eq. (179), of the $\rho(t_0)=\rho_{\text{rot}}(t_0)$ of Eqs. (147) and (152).

The validity of the "master" equation for $P_{\text{rot}}(n;t)$, Eqs. (177) and (178), implies the validity of the corresponding individual particle (here individual spin) "master" equation [see the analogous passage from Eq. (35) to Eqs. (55)–(57) or (64), (65) and then to Eqs. (109)–(111)]

$$\frac{d}{dt}P_{\text{rot};[q]}(\mu_q;t)=\sum_{\mu_q'}[w_{\text{rot};[q]}(\mu_q;\mu_q';t)P_{\text{rot}}(\mu_q';t)-w_{\text{rot};[q]}(\mu_q';\mu_q;t)P_{\text{rot};[q]}(\mu_q;t)], \tag{182}$$

where

$$P_{\text{rot};[q]}(\mu_q;t)\equiv\sum_{\{\mu_i\}^{(q)},\,\eta_i,\,\beta_u}P_{\text{rot}}(n;t)=\sum_{\{\mu_i\}^{(q)},\,\eta_u,\,\beta_u}P_{\text{rot}}(\{\mu_i\};\eta_u,\beta_u;t), \tag{183}$$

$$w_{\text{rot};[q]}(\mu_q;\mu_q';t)\equiv\frac{\displaystyle\sum_{\{\mu_i\}^{(q)},\,\eta_u,\,\beta_u;\,\{\mu_i'\}^{(q)},\,\eta_v,\,\beta_v}W_{\text{rot};n,m}P_{\text{rot}}(m;t)}{\displaystyle\sum_{\{\mu_i'\}^{(q)},\,\eta_v,\,\beta_v}P_{\text{rot}}(m;t)}$$
$$\equiv\frac{\displaystyle\sum_{\{\mu_i\}^{(q)},\,\eta_u,\,\beta_u;\,\{\mu_i'\}^{(q)},\,\eta_v,\,\beta_v}W_{\text{rot}}(\{\mu_i\};\eta_u,\beta_u;\{\mu_i'\},\eta_v,\beta_v)P_{\text{rot}}(\{\mu_i'\};\eta_v,\beta_v;t)}{\displaystyle\sum_{\{\mu_i'\}^{(q)},\,\eta_v,\,\beta_v}P_{\text{rot}}(\{\mu_i'\};\eta_v,\beta_v;t)},$$
$$w_{\text{rot};[q]}(\mu_q';\mu_q;t)\equiv\frac{\displaystyle\sum_{\{\mu_i\}^{(q)},\,\eta_u,\,\beta_u,\,\{\mu_i'\}^{(q)},\,\eta_v,\,\beta_v}W_{\text{rot}}(\{\mu_i'\};\eta_v,\beta_v;\{\mu_i\},\eta_u,\beta_u)P_{\text{rot}}(\{\mu_i\};\eta_u,\beta_u;t)}{\displaystyle\sum_{\{\mu_i\}^{(q)},\,\eta_u,\,\beta_u}P_{\text{rot}}(\{\mu_i\};\eta_u,\beta_u;t)} \tag{184}$$

are, respectively, the probability at time t that the individual spin $[q]$ is found in the state $\phi_{[q]}(\mu_q)$ and the, in general, time dependent individual spin transition probabilities per unit time.

As in the corresponding discussions in Secs. C, E, we can, to a sufficient approximation, replace the quantities $P_{\text{rot}}(\{\mu_i\};\eta_u,\beta_u;t)$, $P_{\text{rot}}(\{\mu_i'\},\eta_v,\beta_v;t)$ in Eq. (184) by their equilibrium values:

$$P_{\text{rot}}^{\text{equil}}(\{\mu_i\},\eta_u,\beta_u;t)=P_{\text{rot}}^{\text{equil}}(\{\mu_i'\},\eta_v,\beta_v;t)=1/\mathfrak{N}=1/\{(2I+1)^{N[A]}\sum_{\eta_v}\mathfrak{N}_{[B]}(\eta_v)\}.$$

These equilibrium values follow from Eqs. (41), (50) since Eqs. (177), (178) are of the same mathematical structure as Eq. (36), or, in more physical language, are a consequence of the "master" equation, Eq. (177), with the "microscopic reversibility" condition, Eq. (178). Thus Eq. (184) becomes, using also Eqs. (178), (179),

$$w_{\text{rot};[q]}(\mu_q;\mu_q';t)\cong w_{\text{rot};[q]}^{\text{equil}}(\mu_q;\mu_q';t)$$
$$=\frac{\displaystyle\sum_{\{\mu_i\}^{(q)},\,\eta_u,\,\beta_u,\,\{\mu_i'\}^{(q)},\,\eta_v,\,\beta_v}(2\pi/\hbar)\delta(\eta_u-\eta_v)\,|\langle\phi_{[A]}(\{\mu_i\})\psi_{[B]}(\eta_u,\beta_u)|\mathcal{V}_{\text{dip-dip}}^{\text{secular}}|\phi_{[A]}(\{\mu_i'\})\psi_{[B]}(\eta_v,\beta_v)\rangle|^2}{\{(2I+1)^{N[A]-1}\sum_{\eta_v}\mathfrak{N}_{[B]}(\eta_v)\}}$$
$$=w_{\text{rot};[q]}^{\text{equil}}(\mu_q';\mu_q;t)\cong w_{\text{rot};[q]}(\mu_q';\mu_q;t), \tag{185}$$

so that "microscopic reversibility" also holds for the $w_{\text{rot};[q]}^{\text{equil}}$.

We now set down typical nonvanishing matrix elements of $\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}$ entering into Eqs. (185) and (182); we find from Eqs. (168), and (179)

$$\langle\{\mu_i\}^{(q),(p)},\mu_q,\mu_p;\eta_u,\beta_u|\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}|\{\mu_i'\}^{(q),(p)};\mu_q-1,\mu_p\mp1;\eta_v,\beta_v\rangle$$
$$=\langle\eta_u;\beta_u|A_{pq}|\eta_v,\beta_v\rangle[(I-\mu_q+1)(I+\mu_q)]^{\frac{1}{2}}\begin{Bmatrix}[(I-\mu_p+1)(I+\mu_p)]^{\frac{1}{2}}\ (\frac{3}{4})\\ [(I-\mu_p)(I+\mu_p+1)]^{\frac{1}{2}}\ (-\frac{1}{4})\end{Bmatrix}. \quad (186)$$

Equations (186) and (185) yield,

$$w_{\text{rot};[q]}{}^{\text{equil}}(\mu_q;\mu_q-1;t)=w_{\text{rot};[q]}{}^{\text{equil}}(\mu_q-1;\mu_q;t)$$
$$=(I-u_q+1)(I+\mu_q)\frac{5}{12}I(I+1)\frac{2\pi}{\hbar}\sum_{\eta_u,\beta_u,\eta_v,\beta_v}\left(\frac{1}{\sum_{\eta_w}\mathfrak{N}_{[B]}(\eta_w)}\right)\delta(\eta_u-\eta_v)\sum_f|\langle\eta_u,\beta_u\rangle|A_{fq}|\eta_v,\beta_v\rangle|^2 \quad (187)$$
$$\equiv(I-\mu_q+1)(I+\mu_q)w_{\text{tran}},$$

which is to be compared with Eqs. (123) and (124) for $w_{[q]}{}^{\text{equil}}(m_q;m_q-1;t)$, $w_{[q]}{}^{\text{equil}}(m_q-1;m_q;t)$. It is to be noted that $A_{fq}=A_{fq}(\mathbf{R}_f+\xi_f-\mathbf{R}_q-\xi_q)$ [Eq. (168)] so that pairs of states $\psi_{[B]}(\eta_v,\beta_v)$, $\psi_{[B]}(\eta_u=\eta_v,\beta_u)$ with nonvanishing $\langle\eta_u=\eta_v,\beta_u|A_{fq}|\eta_v,\beta_v\rangle$, i.e., pairs of states which make finite contributions to $w_{\text{rot};[q]}{}^{\text{equil}}(\mu_q;\mu_q-1;t)$, $w_{\text{rot};[q]}{}^{\text{equil}}(\mu_q-1;\mu_q;t)$, in general contain different numbers of phonons. It is the presence of $\mu_q\rightleftarrows\mu_q-1$ spin flip transitions involving a net phonon emission or absorption which destroys, in the Case (II), the quantal coherence effects so characteristic of Case (I).

Having obtained in Eq. (187) the $w_{\text{rot};[q]}{}^{\text{equil}}(\mu_q;\mu_q';t)$, we can use the methods of Sec. D to solve the individual particle "master" equation, Eq. (182), for $P_{\text{rot};[q]}(\mu_q;t)$. The general procedure is completely analogous to that given in Eqs. (130)–(132), (135)–(142) and will not be reproduced in detail here. With $P_{\text{rot};[q]}(\mu_q;t)$ available and using Eqs. (160), (161), (179), and (183), we can write

$$\langle\mu'\rangle_t=(\hbar\gamma/V_{[A]})\cos[\omega_L(t-t_0)]\sum_{\{\mu_i\},\eta_u,\beta_u}P_{\text{rot}}(\{\mu_i\};\eta_u,\beta_u;t)\left(\sum_{p=1}^{N[A]}\mu_p\right)$$
$$=\cos[\omega_L(t-t_0)]\sum_{p=1}^{N[A]}\sum_{\mu_p=-I}^{I}P_{\text{rot};[p]}(\mu_p;t)(\hbar\gamma\mu_p/V_{[A]})$$
$$=\cos[\omega_L(t-t_0])\sum_{\mu_q=-I}^{I}P_{\text{rot};[q]}(\mu_q;t)\left(\frac{N_{[A]}}{V_{[A]}}\hbar\gamma\mu_q\right), \quad (188)$$

where [analogous to Eq. (130)]

$$P_{\text{rot};[q]}(\mu_q;t)$$
$$=P_{\text{rot};[q]}{}^{\text{equil}}(\mu_q;t)+\sum_{\nu=1}^{2I}K_\nu(\mu_q)e^{-\omega_\nu(t-t_0)}, \quad (189)$$
$$P_{\text{rot};[q]}{}^{\text{equil}}(\mu_q;t)=1/(2I+1),$$

and ω_ν, $K_\nu(m_q)$ are given by Eqs. (131), (132) with $\|w_{[q]}{}^{\text{equil}}\|$, $P_{[q]}(m_q;t)$ replaced by $\|w_{\text{rot};[q]}{}^{\text{equil}}\|$, $P_{\text{rot};[q]}(\mu_q;t)$. Equations (188), (189) yield

$$\langle\mu'\rangle_t=\cos[\omega_L(t-t_0)]\left(\frac{\hbar\gamma N_{[A]}}{V_{[A]}}\right)$$
$$\times\sum_{\nu=1}^{2I}\left(\sum_{\mu_q=-I}^{I}K_\nu(\mu_q)\mu_q\right)e^{-\omega_\nu(t-t_0)}, \quad (190)$$

which is to be compared with Eq. (134) for $\langle\mu\rangle_t$. Equation (190) for $\langle\mu'\rangle_t$ may be used to discuss various special cases, e.g., $I=1$ and $I=\frac{3}{2}$, as in Sec. F for $\langle\mu\rangle_t$. From a fundamental point of view, the nonoscillatory approach of this $\{\langle\mu'\rangle_t/\cos[\omega_L(t-t_0)]\}$ to

$$\{\langle\mu'\rangle_t{}^{\text{equil}}/\cos[\omega_L(t-t_0)]\}=0$$

is to be noted.

A word should be added about the situation in liquids, Here $\mathcal{V}_{\text{dip-dip}}{}^{\text{nonsecular}}(\cdots,\mathbf{r}_f-\mathbf{r}_g,\cdots;\cdots,\mathbf{I}_{[f]},\mathbf{I}_{[g]},\cdots)$ is effectively of the order of

$$\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}(\cdots,\mathbf{r}_f-\mathbf{r}_g,\cdots;\cdots,\mathbf{I}_{[f]},\mathbf{I}_{[g]},\cdots)$$

so Eq. (155) no longer holds and the $\rho_{\text{rot}}(t)$ of Eq. (152) must be used. However the $\rho_{\text{rot}}(t)$ of Eq. (152) does *not* satisfy a relation of the form:

$$\rho_{\text{rot}}(t+\tau)=\exp[-(i/\hbar)\tau\mathcal{L}]\rho_{\text{rot}}(t)\exp[(i/\hbar)\tau\mathcal{L}]$$

—$\mathcal{L}$ some operator—so that the procedure involved in the derivation of Eq. (11) from Eq. (7) and so ultimately in the derivation of the "master" equation, Eq. (35) or Eq. (177), is not immediately applicable. Auxiliary, largely physical, arguments, to be reported elsewhere, show nevertheless that a "master" equation of the type of Eqs. (177), (178), and so an individual particle "master" equation of the type of Eqs. (182)–(185), are also valid in the case of a liquid but with $\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}$ replaced by $\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}+\mathcal{V}_{\text{dip-dip}}{}^{\text{nonsecular}}$ in the corresponding transition probabilities per unit time: $W_{\text{rot};n,m}$, and $w_{\text{rot};[q]}{}^{\text{equil}}(\mu_q;\mu_q';t)$. These $w_{\text{rot}[q]}{}^{\text{equil}}(\mu_q;\mu_q';t)$ may then be evaluated in a manner analogous to that of Eqs. (185)–(187) and the

corresponding $\langle\mu'\rangle_t$ found in a manner analogous to that of Eqs. (188)–(190).

In conclusion, and for the sake of completeness, we most comment briefly on the calculation of expressions involving "lattice" matrix elements such as that entering into Eq. (187):

$$\mathfrak{F}\equiv\frac{2\pi}{\hbar}\sum_{\eta_u,\beta_u,\eta_v,\beta_v}\delta(\eta_u-\eta_v)\frac{\sum_f|\langle\eta_u,\beta_u|A_{fq}|\eta_v,\beta_v\rangle|^2.}{\sum_{\eta_w}\mathfrak{N}_{[B]}(\eta_w)} \quad (191)$$

For solids, A_{fq} can be expanded in terms of the displacements $\xi_f=\mathbf{r}_f-\mathbf{R}_f$, $\xi_q=\mathbf{r}_q-\mathbf{R}_q$ which are known functions of the phonon creation and destruction operators [see Eq. (168)] while β_u, β_v are expressed in terms of the phonon occupation numbers characterizing the states $\psi_{[B]}(\eta_u=\eta_v;\beta_u)$, $\psi_{[B]}(\eta_v,\beta_v)$; thus the matrix elements in $\mathfrak{F}$ and so $\mathfrak{F}$ itself can be evaluated in a reasonably straightforward fashion.[16] On the other hand, in the present state of development the theory of liquids, the $(\mathbf{r}_f-\mathbf{r}_q)$ within A_{fq} cannot in general be expressed in terms of creation and destruction operators of suitable motional quasi-particles and $\mathfrak{F}$ cannot be evaluated exactly. However $\mathfrak{F}$ can be calculated approximately using, eventually, a classical stochastic method.[16] Such a method can be introduced if one recalls the relation

$$\delta(\eta_u-\eta_v)=(1/2\pi\hbar)\int_{-\infty}^{\infty}d\tau\,\exp[(i/\hbar)(\eta_u-\eta_v)\tau], \quad (192)$$

so that

$$\mathfrak{F}=(1/\hbar^2)\sum_f\frac{\int_{-\infty}^{\infty}d\tau\sum_{\eta_u,\beta_u,\eta_v,\beta_v}\langle\eta_u,\beta_u|\mathcal{A}_{fq}(\tau)|\eta_v,\beta_v\rangle\langle\eta_v,\beta_v|\mathcal{A}_{fq}(0)|\eta_u,\beta_u\rangle}{\sum_{\eta_w}\mathfrak{N}_{[B]}(\eta_w)}, \quad (193)$$

where

$$\mathcal{A}_{fq}(\tau)\equiv\exp[(i/\hbar)\tau\mathcal{H}_{[B]}^{(0)}]A_{fq}\times\exp[-(i/\hbar)\tau\mathcal{H}_{[B]}^{(0)}]; \quad (194)$$
$$\mathcal{A}_{fq}(0)=A_{fq}.$$

Thus

$$\mathfrak{F}=\frac{1}{\hbar^2}\sum_f\int_{-\infty}^{\infty}d\tau\left\{\frac{\mathrm{Trace}[\mathcal{A}_{fq}(\tau)\mathcal{A}_{fq}(0)]}{\mathrm{Trace}\ (1)}\right\}. \quad (195)$$

Finally, approximation of the "correlation function of $\mathcal{A}_{fq}(\tau)$,"

$$f(\tau)\equiv\{\mathrm{Trace}[\mathcal{A}_{fq}(\tau)\mathcal{A}_{fq}(0)]/\mathrm{Trace}(1)\},$$

by a suitable average over the quantity $\mathcal{A}_{fq}(\tau)\mathcal{A}_{fq}(0)$, results in the determination of $f(\tau)$ as a known function of τ and permits the evaluation of $\mathfrak{F}$ by calculation of the integral over τ in Eq. (195). In performing this suitable average over $\mathcal{A}_{fq}(\tau)\mathcal{A}_{fq}(0)$ the Heisenberg operators,

$[\mathbf{r}_f(\tau)-\mathbf{r}_q(\tau)]\equiv\exp[(i/\hbar)\tau\mathcal{H}_{[B]}^{(0)}](\mathbf{r}_f-\mathbf{r}_q)$
$\times\exp[-(i/\hbar)\tau\mathcal{H}_{[B]}^{(0)}]$, within the $\mathcal{A}_{fq}(\tau)$ are treated as classical stochastic variables.

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APPENDIX A

In the present appendix, we analyze an example, proposed to us by Norberg, of a supersystem $[A+B]$ described by such an "extremely quantal-coherent" nonequilibrium statistical distribution at the initial time t_0, that $[A+B]$ evolves away from rather than toward the equilibrium statistical distribution. Essentially the same as well as related examples have been analyzed in detail from the point of view of pulsed nuclear magnetic resonance theory[16] by Lowe,[17] and the "solid echoes" observed by Lowe provide experimental evidence for the existence of nonequilibrium statistical distributions which evolve away from equilibrium.

Consider a solid which contains two different nuclear species, A and B. Suppose that the lattice of the solid is effectively rigid (see Sec. G) and that $\gamma_B\gg\gamma_A$ so that the local magnetic field at any nucleus is effectively due only to the B nuclei. Under these circumstances the two spin systems A and B form an essentially self-enclosed supersystem, $[A+B]$ (see related discussion in Sec. G after Eq. (175)) with the A spins acting as the system of interest, $[A]$, and the B spins as the surroundings, $[B]$.

Let us suppose that $[A+B]$ is in equilibrium in a magnetic field $H_{\mathrm{ext}}\hat{z}$ at time $t_0-\tau$ and that at this time a (very short) "90°" rf pulse at a carrier frequency $=\omega_L^{[A]}$ is applied to the A spins. Then, by Eq. (147), we have immediately after application of the "90°" pulse,

$$\rho(t_0-\tau)=\frac{\exp(\hbar\omega_L^{[A]}I_x^{[A]}/\Theta)\exp(\hbar\omega_L^{[B]}I_z^{[B]}/\Theta)}{\mathrm{Trace}\ [\exp(\hbar\omega_L^{[A]}I_x^{[A]}/\Theta)\exp(\hbar\omega_L^{[B]}I_z^{[B]}/\Theta)]}, \quad (A.1)$$

[16] See, for example, the forthcoming book on nuclear magnetic resonance by A. Abragam.
[17] I. J. Lowe, Bull. Am. Phys. Soc. 2, 344 (1957).

while for $t>t_0-\tau$, Eq. (152) yields,

$$\rho_{\rm rot}(t)=\exp[-i(t-t_0+\tau)\omega_L{}^{[A]}I_z{}^{[A]}]\{\exp[i(t-t_0+\tau)(\omega_L{}^{[A]}I_z{}^{[A]}+\omega_L{}^{[B]}I_z{}^{[B]}-(1/\hbar)\mathcal{V})]\rho(t_0-\tau)$$
$$\times\exp[-i(t-t_0+\tau)(\omega_L{}^{[A]}I_z{}^{[A]}+\omega_L{}^{[B]}I_z{}^{[B]}-(1/\hbar)\mathcal{V})]\}\exp[i(t-t_0+\tau)\omega_L{}^{[A]}I_z{}^{[A]}]. \quad (A.2)$$

If now $I_z{}^{[A]}$, $I_z{}^{[B]}$ commute with $\mathcal{V}$, a condition that is satisfied if $\mathcal{V}$ is taken as [see Eqs. (169), (168)],

$$\mathcal{V}=\mathcal{V}_{\text{dip-dip}}{}^{\text{secular}}=\mathcal{V}_{\text{dip }A\text{-dip }A}{}^{\text{secular}}+\mathcal{V}_{\text{dip }B\text{-dip }B}{}^{\text{secular}}+\mathcal{V}_{\text{dip }A\text{-dip }B}{}^{\text{secular}}, \quad (A.3)$$

then

$$\rho_{\rm rot}(t)=\exp[-(i/\hbar)(t-t_0+\tau)\mathcal{V}]\rho(t_0-\tau)\exp[(i/\hbar)(t-t_0+\tau)\mathcal{V}], \quad (A.4)$$

where, in the case at hand [see Eq. (168) and recall that $\hbar\omega_L{}^{[B]}\gg\hbar\omega_L{}^{[A]}$],

$$\mathcal{V}\cong\mathcal{V}_{\text{dip }A\text{-dip }B}{}^{\text{secular}}+\mathcal{V}_{\text{dip }B\text{-dip }B}{}^{\text{secular}}=\sum_{f,g}A_{fg}{}^{[A],[B]}(\mathbf{R}_f-\mathbf{R}_g)(-2I_{[f]z}{}^{[A]}I_{[g]z}{}^{[B]})$$
$$+\tfrac{1}{2}\sum_{g,h}A_{gh}{}^{[B],[B]}(\mathbf{R}_g-\mathbf{R}_h)(I_{[g]x}{}^{[B]}I_{[h]x}{}^{[B]}+I_{[g]y}{}^{[B]}I_{[h]y}{}^{[B]}-2I_{[g]z}{}^{[B]}I_{[h]z}{}^{[B]})$$
$$\equiv-\sum_f\hbar\gamma_A\mathbf{I}_{[f]}{}^{[A]}\cdot\mathbf{H}_{[B]}(\mathbf{R}_f;\cdots\mathbf{I}_{[g]}{}^{[B]}\cdots)-\sum_g\hbar\gamma_B\mathbf{I}_{[g]}{}^{[B]}\cdot\mathbf{H}_{[B]}{}^*(\mathbf{R}_{[g]};\cdots\mathbf{I}_{[h]}{}^{[B]}\cdots). \quad (A.5)$$

Also from Eqs. (154), (160),

$$\langle\mu_{[A]}{}'\rangle_t=(\hbar\gamma_A/V_{[A]})\{\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\,\text{Trace}[\rho_{\rm rot}(t)I_x{}^{[A]}]\}, \quad (A.6)$$

whence, substituting Eq. (A-4) into Eq. (A-6),

$$\langle\mu_{[A]}{}'\rangle_t=(\hbar\gamma_{[A]}/V_{[A]})\{\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\,\text{Trace}(\exp[-(i/\hbar)(t-t_0+\tau)\mathcal{V}]\rho(t_0-\tau)$$
$$\times\exp[(i/\hbar)(t-t_0+\tau)\mathcal{V}]I_x{}^{[A]})\}, \quad (A.7)$$

so that, using also Eq. (A-1),

$$\begin{aligned}\langle\mu_{[A]}{}'\rangle_{t_0-\tau}&=(\hbar\gamma_{[A]}/V_{[A]})\,\text{Trace}\,\{\rho(t_0-\tau)I_x{}^{[A]}\}\\&=(\hbar\gamma_A/V_{[A]})\frac{\text{Trace}\,\{\exp[(\hbar\omega_L{}^{[A]}/\Theta)I_x{}^{[A]}]I_x{}^{[A]}\}}{\text{Trace}\,\{\exp[(\hbar\omega_L{}^{[A]}/\Theta)I_x{}^{[A]}]\}}\\&=\langle\mu_{[A]}\rangle_t{}^{\text{equil}}\cong(N_{[A]}/3V_{[A]})\hbar\gamma_AI^{[A]}(I^{[A]}+1)(\hbar\omega_L{}^{[A]}/\Theta).\end{aligned} \quad (A.8)$$

The Eqs. (A-7) and (A-8) are analogous to Eqs. (175) and (148) and the quantity $\{\langle\mu_{[A]}{}'\rangle_t/\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\}$ will approach $\{\langle\mu_{[A]}{}'\rangle_t{}^{\text{equil}}/\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\}=0$ in an oscillatory fashion—Lowe-Norberg beats; see discussion after Eq. (175) in Sec. G. Thus we may say that the $\rho_{\rm rot}(t)$ of Eq. (A-4) evolves in time as t increases beyond $t_0-\tau$ in such a way that $[A+B]$ approaches equilibrium, though of course, as in the "rigid" lattice case treated in Sec. G, this oscillatory approach to equilibrium as exemplified by the $\{\langle\mu_{[A]}{}'\rangle_t/\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\}$ vs t of Eq. (A-7) cannot be described by any "master" equation.

Let us now suppose that at a time τ after application of the "90°" pulse to the A spins, a (very short) "180°" rf pulse at a carrier frequency $\omega_L{}^{[B]}$ is applied to the B spins. Then, immediately after application of this "180°" pulse, i.e., at the time $(t_0-\tau)+\tau=t_0$, which time t_0 we shall consider as the initial time for the subsequent behavior of $[A+B]$, we have from Eqs. (A-4) and (A-6),

$$\begin{aligned}\rho_{\rm rot}(t_0)&=\exp[i\pi(-I_y{}^{[B]})]\exp[-(i/\hbar)\tau\mathcal{V}]\rho(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}]\exp[-i\pi(-I_y{}^{[B]})]\\&=\exp[-(i/\hbar)\tau\mathcal{V}^*]\rho^*(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}^*],\end{aligned} \quad (A.9)$$

where, using also Eqs. (A-5), (A-1),

$$\mathcal{V}^*\equiv\exp[-i\pi I_y{}^{[B]}]\mathcal{V}\exp[i\pi I_y{}^{[B]}]=-\mathcal{V}_{\text{dip }A\text{-dip }B}{}^{\text{secular}}+\mathcal{V}_{\text{dip }B\text{-dip }B}{}^{\text{secular}}$$

$$\rho^*(t_0-\tau)\equiv\exp[-i\pi I_y{}^{[B]}]\rho(t_0-\tau)\exp[i\pi I_y{}^{[B]}]$$
$$=\frac{\exp[\hbar\omega_L{}^{[A]}I_x{}^{[A]}/\Theta]\exp[-\hbar\omega_L{}^{[B]}I_z{}^{[B]}/\Theta]}{\text{Trace}\,\{\exp[\hbar\omega_L{}^{[A]}I_x{}^{[A]}/\Theta]\exp[-\hbar\omega_L{}^{[B]}I_z{}^{[B]}/\Theta]\}}, \quad (A.10)$$

$$\langle\mu_{[A]}'\rangle_{t_0}/\cos(\omega_L{}^{[A]}\tau)=(\hbar\gamma_A/V_{[A]})\,\mathrm{Trace}\,[\rho(t_0)I_x{}^{[A]}]$$
$$=(\hbar\gamma_{[A]}/V_{[A]})\,\mathrm{Trace}\,\{\exp[-(i/\hbar)\tau\mathcal{V}^*]\rho^*(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}^*]I_x{}^{[A]}\}$$
$$=(\hbar\gamma_{[A]}/V_{[A]})\,\mathrm{Trace}\,\{\exp[-(i/\hbar)\tau\mathcal{V}]\rho(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}]I_x{}^{[A]}\},\tag{A.11}$$

$$\rho_{\mathrm{rot}}(t_0+\tau)=\exp[-(i/\hbar)\tau\mathcal{V}]\rho_{\mathrm{rot}}(t_0)\exp[(i/\hbar)\tau\mathcal{V}]$$
$$=\exp[-(i/\hbar)\tau\mathcal{V}]\exp[-(i/\hbar)\tau\mathcal{V}^*]\rho_{\mathrm{rot}}{}^*(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}^*]\exp[(i/\hbar)\tau\mathcal{V}],\tag{A.12}$$

$$\langle\mu_{[A]}'\rangle_{t_0+\tau}/\cos(2\omega_L{}^{[A]}\tau)=(\hbar\gamma_A/V_{[A]})\,\mathrm{Trace}[\rho_{\mathrm{rot}}(t_0+\tau)I_x{}^{[A]}]$$
$$=(\hbar\gamma_A/V_{[A]})\,\mathrm{Trace}\,[\exp[-(i/\hbar)\tau\mathcal{V}]\exp[-(i/\hbar)\tau\mathcal{V}^*]\rho_{\mathrm{rot}}{}^*(t_0-\tau)$$
$$\times\exp[(i/\hbar)\tau\mathcal{V}^*]\exp[(i/\hbar)\tau\mathcal{V}]I_x{}^{[A]}].\tag{A.13}$$

We now note that [see Eqs. (A-11), (A-8)]

$$\frac{\langle\mu_{[A]}'\rangle_{t_0}/\cos(\omega_L{}^{[A]}\tau)}{\langle\mu_{[A]}'\rangle_{t_0-\tau}}=\frac{\mathrm{Trace}\{\rho(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}]I_x{}^{[A]}\exp[-(i/\hbar)\tau\mathcal{V}]\}}{\mathrm{Trace}\,\{\rho(t_0-\tau)I_x{}^{[A]}\}}$$
$$=1-\tfrac{1}{2}(\tau/\hbar)^2\,\mathrm{Trace}\,\{(\mathcal{V},[\mathcal{V},I_x{}^{[A]}])\}+\cdots\equiv1-\Lambda<1,\tag{A.14}$$

the inequality being, physically speaking, a consequence of the "dephasing effects" of the local fields $\mathbf{H}_{[B]}(\mathbf{R}_f;\cdots\mathbf{I}_g{}^{[B]}\cdots)$ [see Eq. (A-5)] which, in the frame of reference rotating with angular velocity $\omega_L{}^{[A]}\hat{z}$, precess the various A spins, $\mathbf{I}_f{}^{[A]}$, at different rates [since $\mathbf{H}_{[B]}(\mathbf{R}_f;\cdots\mathbf{I}_g{}^{[B]}\cdots)$ is different at different $\mathbf{R}_f$]. The spin "dephasing" Eq. (A-14) which indicates the decrease of $\{\langle\mu_{[A]}'\rangle_t/\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\}$ with t for $t_0-\tau<t<t_0$ is the basis of our previous remark that $[A+B]$ approaches equilibrium during the time interval $t_0-\tau$ to t_0. We further note that [see Eqs. (A-13) and (A-11)],

$$\frac{\langle\mu_{[A]}'\rangle_{t_0+\tau}/\cos(2\omega_L{}^{[A]}\tau)}{\langle\mu_{[A]}'\rangle_{t_0}/\cos(\omega_L{}^{[A]}\tau)}=\frac{\mathrm{Trace}\,\{\rho^*(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}^*]\exp[(i/\hbar)\tau\mathcal{V}]I_x{}^{[A]}\exp[-(i/\hbar)\tau\mathcal{V}]\exp[-(i/\hbar)\tau\mathcal{V}^*]\}}{\mathrm{Trace}\,\{\rho(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}]I_x{}^{[A]}\exp[-(i/\hbar)\tau\mathcal{V}]\}},\tag{A.15}$$

and if the ratio of the traces turns out to be greater than 1, i.e., equal to $1/(1-\Lambda)$, the A spins "rephase" during the time interval t_0 to $t_0+\tau$ and so

$$\langle\mu_{[A]}'\rangle_t/\cos[\omega_L{}^{[A]}(t-t_0+\tau)]$$

increases as a consequence of the reversal of sign of $\mathbf{H}_{[B]}$ by the "180°" pulse, i.e., as a consequence of the difference in sign of the term $\mathcal{V}_{\mathrm{dip}\,A\text{-}\mathrm{dip}\,B}{}^{\mathrm{secular}}$ in $\mathcal{V}^*$ and in $\mathcal{V}$ [Eqs. (A-10) and (A-5)]. Alternatively, if the trace ratio in the spin "rephasing" Eq. (A-15) is greater than 1, i.e., equal to $1/(1-\Lambda)$, we can say that during a time interval of duration τ subsequent to the initial time t_0 the quantity

$$\{\langle\mu_{[A]}'\rangle_t/\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\}$$

evolves further and further from

$$\{\langle\mu_{[A]}'\rangle_t{}^{\mathrm{equil}}/\cos[\omega_L{}^{[A]}(t-t_0+\tau)]\}=0,[18]$$

i.e., during this time interval the nonequilibrium initial statistical distribution of $[A+B]$, described by the $\rho_{\mathrm{rot}}(t_0)$ of Eqs. (A-9) and (A-10), evolves into another statistical distribution, described by the $\rho_{\mathrm{rot}}(t_0+\tau)$ of Eq. (A-12), which is even further from equilibrium. Also we note that, as already mentioned in Sec. B, the nonequilibrium "extremely quantal-coherent" initial $\rho(t_0)$ of Eqs. (A-9), (A-10), and (150) which is associated with this possible trend away from equilibrium is certainly "nondiagonal" with respect to the eigenstates of

$$\mathcal{H}_{[A]}{}^{(0)}+\mathcal{H}_{[B]}{}^{(0)}=-(\hbar\omega_L{}^{[A]}I_z{}^{[A]}+\hbar\omega_L{}^{[B]}I_z{}^{[B]}),$$

viz,

$$\rho(t_0)=\exp[i\tau\omega_L{}^{[A]}I_z{}^{[A]}]\rho_{\mathrm{rot}}(t_0)\exp[-i\tau\omega_L{}^{[A]}I_z{}^{[A]}]$$
$$=\frac{\exp[i\tau(\omega_L{}^{[A]}I_z{}^{[A]}-\hbar^{-1}\mathcal{V}^*)]\exp[\hbar\omega_L{}^{[A]}I_x{}^{[A]}/\Theta]\exp[-i\tau(\omega_L{}^{[A]}I_z{}^{[A]}-\hbar^{-1}\mathcal{V}^*)]\exp[-\hbar\omega_L{}^{[B]}I_z{}^{[B]}/\Theta]}{\mathrm{Trace}\,\{\exp[i\tau(\omega_L{}^{[A]}I_z{}^{[A]}-\hbar^{-1}\mathcal{V}^*)]\exp[\hbar\omega_L{}^{[A]}I_x{}^{[A]}/\Theta]\times\exp[-i\tau(\omega_L{}^{[A]}I_z{}^{[A]}-\hbar^{-1}\mathcal{V}^*)]\exp[-\hbar\omega_L{}^{[B]}I_z{}^{[B]}/\Theta]\}}.\tag{A.16}$$

[18] Because of the assumed rigidity of the lattice containing both the A spins and the B spins, $\langle\mu_{[B]}\rangle_{t_0+\tau}=\langle\mu_{[B]}\rangle_{t_0}=-\langle\mu_{[B]}\rangle_{t_0-\tau}=-\langle\mu_{[B]}\rangle_t{}^{\mathrm{equil}}$, so that, as the A spins "rephase," the B spins effectively remain in the same nonequilibrium (negative temperature) statistical configuration.

It remains to investigate the circumstances under which the ratio of the traces in Eq. (A-15) is actually greater than 1, i.e., equal to $1/(1-\Lambda)$. If the B species is fairly dilute compared to the A species $\mathcal{V}_{\text{dip }B\text{-dip }B}{}^{\text{secular}}$ may be somewhat less important than $\mathcal{V}_{\text{dip }A\text{-dip }B}{}^{\text{secular}}$ so that, from Eqs. (A-10) and (A-5),

$$\mathcal{V}^*\approx -\mathcal{V}. \tag{A.17}$$

Equations (A-17), (A-15), and (A-14) yield

$$\frac{\langle\mu_{[A]}'\rangle_{t_0+\tau}/\cos(2\omega_L{}^{[A]}\tau)}{\langle\mu_{[A]}'\rangle_{t_0}/\cos(\omega_L{}^{[A]}\tau)}=\frac{\text{Trace }\{\rho^*(t_0-\tau)I_x{}^{[A]}\}}{\text{Trace }\{\rho(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}]I_x{}^{[A]}\exp[-(i/\hbar)\tau\mathcal{V}]\}}$$

$$=\frac{\text{Trace }\{\rho(t_0-\tau)I_x{}^{[A]}\}}{\text{Trace }\{\rho(t_0-\tau)\exp[(i/\hbar)\tau\mathcal{V}]I_x{}^{[A]}\exp[-(i/\hbar)\tau\mathcal{V}]\}}$$

$$=\frac{\langle\mu_{[A]}'\rangle_{t_0-\tau}}{\langle\mu_{[A]}'\rangle_{t}/\cos(\omega_L{}^{[A]}\tau)}=\frac{1}{1-\Lambda}>1, \tag{A.18}$$

which shows that, in the approximation of Eq. (A-17), the "dephasing" of the A spins during the time interval $t_0-\tau$ to t_0 is wholly compensated by their "rephasing" during the time interval t_0 to $t_0+\tau$. In practice however it is probably a poor approximation, even at small dilutions of B, to neglect the "dephasing" $\mathcal{V}_{\text{dip }B\text{-dip }B}{}^{\text{secular}}$ compared to the "rephasing" $\mathcal{V}_{\text{dip }A\text{-dip }B}{}^{\text{secular}}$ so that the actual "rephasing" of the A spins is far from complete.

APPENDIX B

In this appendix we present the solution of Eq. (75) by a Laplace transform method and discuss further certain mathematical questions mentioned in Sec. D.

Let $p(n;s)$ be the Laplace transform of $P(n;t)$

$$p(n;s)=\int_{t_0}^{\infty}e^{-s(t-t_0)}P(n;t)dt. \tag{B.1}$$

Then, the Laplace transform of Eq. (75) is

$$s\|p(s)\|-\|P(t_0)\|=\|W\|\cdot\|p(s)\|, \tag{B.2}$$

or

$$(s\|1\|-\|W\|)\cdot\|p(s)\|=\|P(t_0)\|. \tag{B.3}$$

The solution of the N linear inhomogeneous equations specified by Eq. (B-3) can be written as,

$$p(n;s)=C(n,s)/D(s), \tag{B.4}$$

where

$$D(s)=\det\{s\|1\|-\|W\|\}$$

$$=\det\begin{vmatrix} s-T_1{}^{-1} & -W_{12} & \cdots & -W_{1N}\\ -W_{21} & s-T_2{}^{-1} & \cdots & -W_{2N}\\ \vdots & \vdots & & \vdots\\ -W_{N1} & -W_{N2} & \cdots & s-T_N{}^{-1}\end{vmatrix}, \tag{B.5}$$

and $C(n;s)$ is the same determinant as $D(s)$ except that the terms in the nth column are replaced by $P(n';t_0)$, $n'=1, 2, 3, \cdots, N$. $D(s)$ can be written in the factored form:

$$D(s)=(s+\omega_0)(s+\omega_1)(s+\omega_2)\cdots(s+\omega_{N-1}), \tag{B.6}$$

where the $-\omega_\nu$; $\nu=0, 1, 2, \cdots, N-1$ are the roots of the polynomial $D(s)$, and in view of Eq. (B-5), are also the eigenvalues of $\|W\|$.

Since $C(n;s)$ is a polynomial of order $N-1$, the method of partial fractions can be used to give:

$$p(n;s)=\sum_{\nu=0}^{N-1}\frac{K_\nu(n)}{s+\omega_\nu}, \tag{B.7}$$

for nondegenerate ω_ν, where,

$$K_\nu(n)=C(n;-\omega_\nu)\Big/\prod_{\nu'=0;(\nu'\neq\nu)}^{N-1}(\omega_{\nu'}-\omega_\nu)$$

$$=C(n;-\omega_\nu)\Big/\frac{dD(s)}{ds}\bigg|_{s=-\omega_\nu}, \tag{B.8}$$

so that

$$\|K_\nu\|=\left\{\left[\frac{1}{\dfrac{dD(s)}{ds}}\right]\begin{Vmatrix}C(1;s)\\ C(2;s)\\ \vdots\\ C(N;s)\end{Vmatrix}\right\}_{s=-\omega_\nu}. \tag{B.9}$$

The inverse Laplace transform of Eq. (B-7) reproduces Eqs. (81), (104), and (105).

Let us now briefly treat the degenerate case where $\omega_\nu=\omega_{\nu'}$ for certain ν and ν'. Here

$$D(s)=\prod_{\nu=0}^{N_d-1}(s+\omega_\nu)^{r_\nu};\quad \sum_{\nu=0}^{N_d-1}r_\nu=N, \tag{B.10}$$

where N_d is the number of distinct ω_ν, $(N_d\leqq N)$. With this $D(s)$ the method of partial fractions leads to the following generalization of Eqs. (B-7), (B-8):

$$p(n,s)=\sum_{\nu=0}^{N_d-1}\sum_{j=1}^{r_\nu}\frac{K_{\nu j}(n)}{(s+\omega_\nu)^j}, \tag{B.11}$$

where

$$K_{\nu j}(n)=\frac{d^{(r_\nu-j)}\phi_\nu(n,s)}{ds^{(r_\nu-j)}}\bigg]_{s=-\omega_\nu}\Big/(r_\nu-j)!, \tag{B.12}$$

with

$$\phi_\nu(n,s)=(s+\omega_\nu)^{r_\nu}\frac{C(n;s)}{D(s)}. \quad \text{(B.13)}$$

The inverse Laplace transform of the $p(n,s)$ of Eq. (B-11) is:

$$P(n;t)=\sum_{\nu=0}^{Nd-1}\sum_{j=1}^{r_\nu}\frac{K_{\nu j}(n)}{(j-1)!}t^{(j-1)}e^{-\omega_\nu(t-t_0)}, \quad \text{(B.14)}$$

i.e.,

$$\|P(t)\|=\sum_{\nu=0}^{Nd-1}\sum_{j=1}^{r_\nu}\frac{\|K_{\nu j}\|}{(j-1)!}t^{(j-1)}e^{-\omega_\nu(t-t_0)} \quad \text{(B.15)}$$

which is the appropriate generalization of Eq. (81) to the case of degenerate ω_ν.

APPENDIX C

The evolution in time of $\langle\mu\rangle_t$ toward $\langle\mu\rangle_t^{\text{equil}}$ [as in Eqs. (137)–(139), (142), (145)] has also been treated in terms of the concept of a time-dependent "spin-temperature" $T_s(t)$. In the spin-temperature procedure, solutions of the individual particle "master" equation, Eq. (110), having the form,

$$P_{[q]}(m_q;t)=\frac{\exp[-\epsilon_{[q]}(m_q)/kT_s(t)]}{\sum_{m_q}\exp[-\epsilon_{[q]}(m_q)/kT_s(t)]}\cong\frac{1+m_q(\hbar\omega_L/kT_s(t))}{(2I+1)}, \quad \text{(C.1)}$$

are assumed, whence, substitution of Eq. (C-1) into Eq. (110) and use of Eq. (115) yields

$$\frac{d}{dt}\left[\ln\left(\frac{1}{T_s(t)}-\frac{1}{T}\right)\right]=-\left[\sum_{m_q'}w_{[q]}{}^{\text{equil}}(m_q';m_q;t)\left(1-\frac{m_q'}{m_q}\right)\right]\equiv-\omega(m_q);$$

$$m_q\neq 0, \quad \text{(C.2)}$$

$$0=\sum_{m_q'}w_{[q]}{}^{\text{equil}}(m_q';0;t)m_q'\equiv\nu;$$

$$m_q=0 \quad (\text{only when } I=1,2,3,\cdots).$$

Equations (C.2) and (C.1) give

$$\begin{aligned}P_{[q]}(m_q;t)&=\frac{1}{2I+1}+\frac{m_q}{2I+1}\frac{\hbar\omega_L}{k}\left[\frac{1}{T}+\left(\frac{1}{T_s(t_0)}-\frac{1}{T}\right)e^{-\omega(m_q)(t-t_0)}\right]\\&=P_{[q]}{}^{\text{equil}}(m_q;t)+\frac{\hbar\omega_L}{(2I+1)k}m_q\left(\frac{1}{T_s(t_0)}-\frac{1}{T}\right)e^{-\omega(m_q)(t-t_0)},\end{aligned} \quad \text{(C.3)}$$

which is to be compared with the $P_{[q]}(m_q;t)$ of Eqs. (130)–(132).

It is now to be emphasized that Eq. (C-3) for $P_{[q]}(m_q;t)$ is correct and so is equivalent to Eqs. (130)–(132) for $P_{[q]}(m_q;t)$ only if Eq. (C-2) is satisfied, i.e., only if the transition probabilities per unit time, $w_{[q]}{}^{\text{equil}}(m_q';m_q;t)$ are such that $\nu=0$ and that the $\omega(m_q)$ are actually independent of m_q (for $m_q\neq 0$); this last condition must hold since $(1/T_s(t)-1/T)$ is independent of m_q. Using Eqs. (123), (124), (126)–(129) with $\hbar\omega_L/\Theta\ll 1$ it is straightforward to verify that the $w_{[q]}{}^{\text{equil}}(m_q';m_q;t)$ are indeed such that $\nu=0$ always, and that the $\omega(m_q)$ are independent of m_q (for $m_q\neq 0$) for $\mathcal{V}=\mathcal{V}_{\text{dip-dip}}{}^{\text{nonsecular}}$ with any I, and for $\mathcal{V}_{\text{quad}}{}^{\text{nonsecular}}$ with $I=1$; in fact:

$$\omega(m_q)=2w:\quad \mathcal{V}=\mathcal{V}_{\text{dip-dip}}{}^{\text{nonsecular}};\quad I=1,\tfrac{3}{2},$$
$$\text{(Cases I, II of Sec. F)},\ I>\tfrac{3}{2} \quad \text{(C.4)}$$

$$\omega(m_q)=2w'+8w'':\quad \mathcal{V}=\mathcal{V}_{\text{quad}}{}^{\text{nonsecular}};\quad I=1$$
$$\text{(Case III of Sec. F)}.$$

On the other hand, for $\mathcal{V}_{\text{quad}}{}^{\text{nonsecular}}$ and $I>1$,

$$\omega(m_q)=2w'[1+8m_q^2-4I(I+1)]+8w''[2I(I+1)-2m_q^2-1], \quad \text{(C.5)}$$

so that for $\mathcal{V}=\mathcal{V}_{\text{quad}}{}^{\text{nonsecular}}$ with $I>1$ the spin-temperature $P_{[q]}(m_q;t)$ of Eq. (C-3) are *not* correct.

Confining our further attention to the cases of Eq. (C-4), where the $P_{[q]}(m_q;t)$ of Eq. (C-3) are correct and so are equivalent to the $P_{[q]}(m_q;t)$ of Eqs. (130)–(132), let us substitute the $P_{[q]}(m_q;t)$ of Eq. (C-3) into Eq. (133) and obtain,

$$\begin{aligned}\langle\mu\rangle_t&=\sum_{m_q}P_{[q]}(m_q;t)\left(\frac{N_{[A]}}{V_{[A]}}\hbar\gamma m_q\right)\\&=\langle\mu\rangle_t{}^{\text{equil}}\{1-[1-T/T_s(t_0)]e^{-\omega(t-t_0)}\};\end{aligned} \quad \text{(C.6)}$$

$$\langle\mu\rangle_t{}^{\text{equil}}\cong(N_{[A]}/V_{[A]})\tfrac{1}{3}\hbar\gamma I(I+1)(\hbar\omega_L/\Theta),$$

which, for example in the condition of initial saturation, $T_s(t_0)=\infty$, becomes,

$$\langle\mu\rangle_t=\langle\mu\rangle_t{}^{\text{equil}}[1-e^{-\omega(t-t_0)}]. \quad \text{(C.7)}$$

The Eqs. (C-7) and (C-4) for $\langle\mu\rangle_t$ are identical with the Eqs. (138), (142), and (145) for $\langle\mu\rangle_t$ vs t.