$$\int_{s_0}^{s_1}\int_{s_0}^{s_1} dsds'|K_l'(s,s')|^2<\infty.$$

The upper limit is the dangerous point, but as long as $a_l<\frac{1}{2}$ we see from Eq. (II.23) that there is no trouble. The Fredholm form has indeed been restored.

Perhaps the most immediate subsequent question is whether our new kernel $K_l'(s,s')$ is holomorphic in l over the same domain as $B_l{}^P(s)$. This is equivalent to the corresponding question about $O_l(s,s')$, which then leads us to an examination of (II.22). Evidently, as long as $0<\lambda_l<1$, so that $\mathrm{Im}k_{2l}>\mathrm{Im}k_{1l}$, we are dealing with an analytic function of l wherever λ_l as given by (I.5) is analytic. Now it will certainly happen that, for some choices of s_1 or some guesses about Regge trajectories and residues for the crossed channels, we shall find from the formulas of reference 1 that $\lambda_l>1$ or $\lambda_l<0$ for some $\mathrm{Re}l\gtrsim0$. When this catastrophe occurs, however, it is a sign either that we have made a bad guess or that the aforementioned formulas are insufficiently accurate, because in an exact calculation unitarity requires $0\leqslant\lambda_l\leqslant1$. Thus, if physically reasonable solutions of the strip equations can be found they will have the property that the only singularities in the right half l plane are Regge poles, arising from the zeros of $D_l(s)$. It is expected that $B_l{}^P(s)$ and, therefore, λ_l has fixed singularities in the left half l plane. By analogy with potential scattering one might expect Regge trajectories to terminate at these points, but the continuation based on our approximate equations must fail somewhat sooner, when λ_l exceeds the unitarity bounds.

It follows, incidentally, from the manner in which our N/D equations have been constructed that both $\mathrm{Re}B_l(s)$ and $\mathrm{Im}B_l(s)$ are continuous through the point s_1. In a one-channel approximation this means that the inelastic cross section vanishes at $s=s_1$ and rises gradually to the correct Regge limit. If a generalization of the equations in this paper to several two-body channels can be made, a more realistic inelastic threshold can be achieved.

ACKNOWLEDGMENTS

Extremely helpful discussions with K. Wilson, F. Smithies, E. Squires, and J. R. Taylor are gratefully acknowledged.

PHYSICAL REVIEW VOLUME 130, NUMBER 3 1 MAY 1963

Approach to Equilibrium in Quantal Systems. II. Time-Dependent Temperatures and Magnetic Resonance

A. Sher*†
Varian Associates, Palo Alto, California

AND

H. Primakoff†‡
University of Pennsylvania, Philadelphia, Pennsylvania

(Received 4 December 1962)

The present paper contains an extension and generalization of results in a previous paper on the basis of the master equation for the approach to equilibrium of a system of interest. The concept of quasi-equilibrium of the system of interest associated with a time-dependent temperature is introduced and is then applied to a description of the processes of longitudinal and transverse relaxation in magnetic resonance and to a discussion of the law of entropy variation. Systems of interest of "size" comparable to their surroundings are consistently included in the treatment.

I. INTRODUCTION

In a previous paper[1] the "master" or Boltzmann "gain-loss" equation was derived from the Schrödinger equation for an isolated "supersystem" [$A+B$] composed of a "system of interest" [A] in relatively weak interaction with a larger system called the "surroundings" [B]. The random phase assumption was required for the state of the supersystem [$A+B$] at the *initial* time only. The Hamiltonian $\mathcal{H}$ of such a supersystem is

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

where $\mathcal{H}_{[A]}{}^{(0)}$ contains only [A] system dynamical variables, $\mathcal{H}_{[B]}{}^{(0)}$ only [B] dynamical system variables, and V dynamical variables of both systems. A master equation for the occupation probabilities of the system of interest was then derived in I under the assumption that the surroundings [B] have a large internal energy com-

* Some of this work was done while the author was a National Science Foundation Postdoctoral Fellow at C.E.N. de Saclay, 1960–1961.

† Part of this work was done while the authors were members of the Physics Division of the Aspen Institute of Humanistic Studies.

‡ The work of this author is supported in part by the National Science Foundation.

[1] A. Sher and H. Primakoff, Phys. Rev. **119**, 178 (1960). This paper will be referred to as I in the present work.

pared to that of the system of interest $[A]$ ($[B]\gg[A]$). Finally, a master equation was derived for individual particle states in situations where the particles could be treated as effectively independent, and several applications were discussed.

This previous work did not, however, take explicit account of interactions which connect different states of the system of interest with the same energy. The purpose of the present paper is to include such interactions in some detail, to treat situations where the internal energy of $[B]$ is not necessarily large compared to $[A]$ ($[B]\approx[A]$), and to consider various other extensions and generalizations of the results obtained in I.

To make the problem more definite we can write, in a notation only slightly modified from that of I,

$$\mathcal{H}_{[A]}^{(0)}\psi_{[A]}(\epsilon_u,\alpha_u)=\epsilon_u\psi_{[A]}(\epsilon_u,\alpha_u),$$
$$\mathcal{H}_{[B]}^{(0)}\psi_{[B]}(\eta_u,\beta_u)=\eta_u\psi_{[B]}(\eta_u,\beta_u),$$

where the states of the $[A]$ system, $\psi_{[A]}(\epsilon_u,\alpha_u)$, are specified by their energy ϵ_u and by other quantum numbers α_u which distinguish among the various degenerate states with energy ϵ_u; we have $\alpha_u=1,\,2,\,\cdots,\,\mathfrak{N}_{[A]}(\epsilon_u)$ where $\mathfrak{N}_{[A]}(\epsilon_u)$ is the number of $[A]$ energy eigenstates with energy eigenvalue ϵ_u. The states of the $[B]$ system, $\psi_{[B]}(\eta_u,\beta_u)$, are defined analogously. The interaction V effects transitions among mutually accessible supersystem states $\psi_{[A]}(\epsilon_u,\alpha_u)\cdot\psi_{[B]}(\eta_u,\beta_u)$, $\psi_{[A]}(\epsilon_v,\alpha_v)\cdot\psi_{[B]}(\eta_v,\beta_v)$ with the same total energy $\epsilon_u+\eta_u=\epsilon_v+\eta_v=E$.

The interaction V can be divided, for our purpose, into a sum of three kinds of terms:

$$V=V_{[A]}+V_{[B]}+V_{[AB]}\equiv V_{[A]}+V_{[B]}+V_{[AB]}^{\text{secular}}+V_{[AB]}^{\text{nonsecular}} \tag{2}$$

where $V_{[A]}$ and $V_{[B]}$ depend only on dynamical variables of $[A]$ and $[B]$, respectively, $V_{[AB]}$ depends on dynamical variables from both $[A]$ and $[B]$, and

$$\begin{gathered}[\mathcal{H}_{[A]}^{(0)},V_{[A]}]=0;\qquad [\mathcal{H}_{[B]}^{(0)},V_{[B]}]=0;\qquad [\mathcal{H}_{[A]}^{(0)},V_{[AB]}^{\text{secular}}]=0;\\ [\mathcal{H}_{[B]}^{(0)},V_{[AB]}^{\text{secular}}]=0;\quad [\mathcal{H}_{[A]}^{(0)},V_{[AB]}^{\text{nonsecular}}]\neq0;\quad [\mathcal{H}_{[B]}^{(0)},V_{[AB]}^{\text{nonsecular}}]\neq0.\end{gathered} \tag{3}$$

The various developments below will also necessitate the assumptions:

$$\mathcal{H}_{[A]}^{(0)}\gg V_{[A]},\ V_{[AB]}^{\text{secular}};\quad \mathcal{H}_{[B]}^{(0)}\gg V_{[B]},\ V_{[AB]}^{\text{secular}};\quad \mathcal{H}_{[A]}^{(0)}+\mathcal{H}_{[B]}^{(0)}\gg V_{[AB]}^{\text{nonsecular}}.$$

Suppose now that, in addition, $V_{[A]}$, $V_{[B]}$, $V_{[AB]}^{\text{secular}}$, $V_{[AB]}^{\text{nonsecular}}$, are such that[2]

$$\begin{aligned}\langle\epsilon_u,\alpha_u;\eta_u,\beta_u|V_{[A]}|\epsilon_u,\alpha_u';\eta_u,\beta_u\rangle&\neq0,\quad \text{for all }\alpha_u,\ \alpha_u'\text{ with }\alpha_u\neq\alpha_u';\\ \langle\epsilon_u,\alpha_u;\eta_u,\beta_u|V_{[B]}|\epsilon_u,\alpha_u;\eta_u,\beta_u'\rangle&\neq0,\quad \text{for all }\beta_u,\ \beta_u'\text{ with }\beta_u\neq\beta_u';\\ \langle\epsilon_u,\alpha_u;\eta_u,\beta_u|V_{[AB]}^{\text{secular}}|\epsilon_u,\alpha_u';\eta_u,\beta_u'\rangle&\neq0,\quad \text{for all }\alpha_u,\ \alpha_u'\text{ and }\beta_u,\ \beta_u'\\ &\qquad\qquad \text{with }\beta_u\neq\beta_u'\text{ if }\alpha_u=\alpha_u'\text{ and }\alpha_u\neq\alpha_u'\text{ if }\beta_u=\beta_u';\\ \langle\epsilon_u,\alpha_u;\eta_u,\beta_u|V_{[AB]}^{\text{nonsecular}}|\epsilon_u,\alpha_u';\eta_u,\beta_u'\rangle&=0,\quad \text{for all }\alpha_u,\ \alpha_u'\text{ and }\beta_u,\ \beta_u'.\end{aligned} \tag{4}$$

Then, since Eq. (3) implies that $\langle\epsilon_u,\alpha_u;\eta_u,\beta_u|V_{[A]}|\epsilon_v,\alpha_v;\eta_u,\beta_u\rangle=0$ for all $v\neq u$ (and similarly for corresponding matrix elements of $V_{[B]}$, $V_{[AB]}^{\text{secular}}$) and $\langle\epsilon_u,\alpha_u;\eta_u,\beta_u|V_{[AB]}^{\text{nonsecular}}|\epsilon_v,\alpha_v;\eta_v,\beta_v\rangle\neq0$ for all $v\neq u$, the interactions $V_{[A]}$, $V_{[B]}$, $V_{[AB]}^{\text{secular}}$ do not exchange energy between the $[A]$ system and the $[B]$ system such energy exchanges being effected only by the interaction $V_{[AB]}^{\text{nonsecular}}$. On the other hand, one can see from Eq. (4), that the interactions $V_{[A]}$, $V_{[B]}$, $V_{[AB]}^{\text{secular}}$ do have a tendency to equalize the occupation probabilities[3] $P_{[A]}(\epsilon_u,\alpha_u;t)$ and $P_{[A]}(\epsilon_u,\alpha_u';t)$; $P_{[B]}(\eta_u,\beta_u;t)$ and $P_{[B]}(\eta_u,\beta_u';t)$. Thus, while the interactions $V_{[A]}$, $V_{[B]}$, $V_{[AB]}^{\text{secular}}$ do not contribute to the time rate of change of $\langle\epsilon\rangle_t\equiv\sum_{\epsilon_u,\alpha_u}\epsilon_uP_{[A]}(\epsilon_u,\alpha_u;t)$, they nonetheless do play a crucial role in determining the nonequilibrium values of $P_{[A]}(\epsilon_u,\alpha_u;t)$, $P_{[B]}(\eta_u,\beta_u;t)$, as will be discussed in detail below.

From the point of view of the individual particle states[4] within the system of interest $[A]$ we shall show [see especially Eqs. (17), (18), (32)–(45), (70), below] that the transitions induced by the interactions $V_{[A]}$, $V_{[AB]}^{\text{secular}}$ tend to establish and maintain a *quasi-equilibrium* occupation probability distribution for the $[q]$th individual particle $P_{[q]}^{\text{quasi-equil }[A]}(u^{(q)};t)\equiv P_{[q]}^{\text{quasi-equil }[A]}(\epsilon(u^{(q)}),\alpha(u^{(q)});t)$ characterized by a time-dependent temperature $\Theta_{[A]}(t)\equiv kT_{[A]}(t)$:

$$P_{[q]}^{\text{quasi-equil }[A]}(u^{(q)};t)\equiv P_{[q]}^{\text{quasi-equil }[A]}(\epsilon(u^{(q)}),\alpha(u^{(q)});t)\equiv \sum_{\substack{\text{all states of every}\\ \text{particle but the }[q]\text{th}}} P_{[A]}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u;t)$$
$$\equiv\sum_{\{u^{(i)}\}^{(q)}} P_{[A]}^{\text{quasi-equil }[A]}(\{u^{(i)}\};t)=e^{-\epsilon(u^{(q)})/\Theta_{[A]}(t)}\Big/\Big\{\sum_{u^{(q)}} e^{-\epsilon(u^{(q)})/\Theta_{[A]}(t)}\Big\}, \tag{5}$$

[2] The necessity of this condition was pointed out to one of us (A. S.) by Professor A. Abragam.
[3] See Eq. (I-55).
[4] See Eqs. (I-108) and (I-109).

where

$$\epsilon_u,\alpha_u \equiv \epsilon(\{u^{(i)}\}), \alpha(\{u^{(i)}\}); \{u^{(i)}\} \equiv u^{(1)}, u^{(2)}, \cdots, u^{(i)}, \cdots, u^{(q-1)}, u^{(q)}, u^{(q+1)}, \cdots,$$
$$\{u^{(i)}\}^{(q)} \equiv u^{(1)}, u^{(2)}, \cdots, u^{(i)}, \cdots, u^{(q-1)}, u^{(q+1)}, \cdots, \tag{6}$$

and where we have neglected the effect of symmetry or antisymmetry of the many-particle wave function of [A] (Boltzmann statistics). We shall also show [see Eqs. (36)–(45), Eq. (18) *et seq.*, below] that $dT_{[A]}(t)/dt$ is governed by the strength of the interaction $V_{[AB]}{}^{\text{nonsecular}}$ which exchanges energy between the system of interest [A] and the surroundings (heat bath) [B] so that eventually $T_{[A]}(t)$ becomes equal to the ultimate and time-persistent equilibrium temperature common to both [A] and [B].

II. THE MASTER EQUATION FOR THE SYSTEM OF INTEREST [A]

To derive the master equation for the system of interest we begin with the master equation for the supersystem[5]:

$$\frac{dP_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)}{dt} = \sum_{\epsilon_v,\alpha_v;\eta_v,\beta_v} [W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_v,\alpha_v;\eta_v,\beta_v)P_{[A+B]}(\epsilon_v,\alpha_v;\eta_v,\beta_v;t)$$
$$-W_{[A+B]}(\epsilon_v,\alpha_v;\eta_v,\beta_v/\epsilon_u,\alpha_u;\eta_u,\beta_u)P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)], \tag{7}$$

where

$$W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_v,\alpha_v;\eta_v,\beta_v) = W_{[A+B]}(\epsilon_v,\alpha_v;\eta_v,\beta_v/\epsilon_u,\alpha_u;\eta_u,\beta_u) = \frac{2\pi}{\hbar}\delta(\epsilon_u+\eta_u-\epsilon_v-\eta_v)\,|\langle\epsilon_u,\alpha_u;\eta_u,\beta_u|\,V_{[A]}$$
$$+V_{[B]}+V_{[AB]}{}^{\text{secular}}+V_{[AB]}{}^{\text{nonsecular}}\,|\,\epsilon_v,\alpha_v;\eta_v,\beta_v\rangle|^2. \tag{8}$$

In Eqs. (7) and (8), $P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)$ is the occupation probability at time t of the supersystem state: $\psi_{[A]}(\epsilon_u,\alpha_u)\cdot\psi_{[B]}(\eta_u,\beta_u)$ and $W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_v,\alpha_v;\eta_v,\beta_v)$ is the probability per unit time for transition of the supersystem from the state $\psi_{[A]}(\epsilon_v,\alpha_v)\cdot\psi_{[B]}(\eta_v,\beta_v)$ to the state $\psi_{[A]}(\epsilon_u,\alpha_u)\cdot\psi_{[B]}(\eta_u,\beta_u)$.

Let us first assume that $V_{[B]}\gg V_{[A]}+V_{[AB]}{}^{\text{secular}}+V_{[AB]}{}^{\text{nonsecular}}$, a situation which can occur not only when $[B]\gg[A]$, but also when $[B]\approx[A]$. Equation (7) may then be written as

$$\frac{d}{dt}P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)$$
$$=\sum_{\beta_u'} W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_u,\alpha_u;\eta_u,\beta_u')[P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u';t)-P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)]$$
$$+\sum_{\alpha_u',\beta_u'} W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_u,\alpha_u';\eta_u,\beta_u')[P_{[A+B]}(\epsilon_u,\alpha_u';\eta_u,\beta_u';t)-P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)]$$
$$+\sum_{\epsilon_v,\alpha_v;\eta_v,\beta_v(v\neq u)} W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_v,\alpha_v;\eta_v,\beta_v)[P_{[A+B]}(\epsilon_v,\alpha_v;\eta_v,\beta_v;t)-P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)], \tag{9}$$

with [see Eqs. (8), (4), and (3)]

$$W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_u,\alpha_u;\eta_u,\beta_u')\gg W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_u,\alpha_u';\eta_u,\beta_u')\quad(\alpha_u\neq\alpha_u'),$$
$$\gg W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_v,\alpha_v;\eta_v,\beta_v)\quad(v\neq u). \tag{10}$$

Thus, the statistical configuration of the supersystem [$A+B$] associated with the *quasi-equilibrium* of the surroundings [B] is described by

$$P_{[A+B]}{}^{\text{quasi-equil }[B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)=P_{[A+B]}{}^{\text{quasi-equil }[B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u';t);\ t-t_0\gtrsim T_{\text{quasi-equil }[B]}, \tag{11}$$

a condition which renders the first term on the right side of Eq. (9) equal to zero—it will be noted from Eq. (10) that if Eq. (11) is not satisfied this first term is generally large and so produces a large $(d/dt)P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)$. In this way, Eqs. (9)–(11) demonstrate that in cases where $V_{[B]}\gg V_{[A]}+V_{[AB]}{}^{\text{secular}}+V_{[AB]}{}^{\text{nonsecular}}$ the occupation probabilities $P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)$ first relax relatively rapidly toward the $P_{[A+B]}{}^{\text{quasi-equil }[B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)$ of Eq. (11) and then approach more slowly the ultimate and time-persistent equilibrium values[6]: $P_{[A+B]}{}^{\text{equil}}(\epsilon_u,\alpha_u;\eta_u,\beta_u)=P_{[A+B]}{}^{\text{equil}}(\epsilon_v,\alpha_v;\eta_v,\beta_v)=1/\mathfrak{N}_{[A+B]}(E)$; it should also be emphasized that Eq. (11) shows that the $P_{[A+B]}{}^{\text{quasi-equil }[B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)$ are actually independent of β_u.[7]

[5] See Eqs. (I-35), (I-36), and (I-54).

[6] See Eqs. (I-41), (I-50), and (I-54); $\mathfrak{N}_{[A+B]}(E)$ is the number of mutually accessible states of [$A+B$].

[7] In I [see discussion after Eq. (I-63)] the $P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)$ are shown to be independent of β_u if $[B]\gg[A]$ and provided that [B] is in equilibrium; our present discussion leading up to Eq. (11) establishes this same independence even if $[B]\approx[A]$ provided that $t-t_0\gtrsim T_{\text{quasi-equil }[B]}$.

We now proceed to a derivation of the master equation for the system of interest $[A]$. Using Eq. (7) and following the procedure of Eqs. (I-53)–(I-62), we have for the time rate of change of the system of interest's occupation probability:

$$\frac{d}{dt}P_{[A]}(\epsilon_u,\alpha_u;t)\equiv\frac{d}{dt}\sum_{\eta_u,\beta_u}P_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u;t)=\frac{d}{dt}\sum_{\beta_u}P_{[A+B]}(\epsilon_u,\alpha_u;E-\epsilon_u,\beta_u;t)$$
$$=\sum_{\epsilon_v,\alpha_v}[W_{[A]}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v;t)P_{[A]}(\epsilon_v,\alpha_v;t)-W_{[A]}(\epsilon_v,\alpha_v/\epsilon_u,\alpha_u;t)P_{[A]}(\epsilon_u,\alpha_u;t)],\quad(12)$$

with $W_{[A]}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v;t)$ given in terms of $W_{[A+B]}(\epsilon_u,\alpha_u;\eta_u,\beta_u/\epsilon_v,\alpha_v;\eta_v,\beta_v)$ by Eq. (I-57). This last equation also shows that the $W_{[A]}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v;t)$ are actually independent of time t if the $P_{[A+B]}(\epsilon_v,\alpha_v;\eta_v,\beta_v;t)$ are independent of β_v.[7] Thus, in light of Eq. (11) *et seq.*, we see that once the quasi-equilibrium statistical configuration of $[B]$ is attained, the corresponding system of interest transition probabilities $W_{[A]}{}^{\text{quasi-equil }[B]}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v;t)$ are actually independent of time t, and are in fact equal to their ultimate and time-persistent equilibrium values, i.e., $W_{[A]}{}^{\text{quasi-equil }[B]}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v;t)=W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v)$ for $t-t_0\gtrsim T_{\text{quasi-equil }[B]}$. Equation (12) and Eqs. (I-60)–(I-62) then give

$$\frac{P_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u)}{P_{[A]}{}^{\text{equil}}(\epsilon_v,\alpha_v)}=\frac{W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v)}{W_{[A]}{}^{\text{equil}}(\epsilon_v,\alpha_v/\epsilon_u,\alpha_u)}=\frac{\mathfrak{N}_{[B]}(E-\epsilon_u)}{\mathfrak{N}_{[B]}(E-\epsilon_v)},\quad(13)$$

and Eq. (12) becomes for $t-t_0\gtrsim T_{\text{quasi-equil }[B]}$:

$$\frac{d}{dt}P_{[A]}(\epsilon_u,\alpha_u;t)=\sum_{\alpha_u'}W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_u,\alpha_u')[P_{[A]}(\epsilon_u,\alpha_u';t)-P_{[A]}(\epsilon_u,\alpha_u;t)]$$
$$+\sum_{\epsilon_v,\alpha_v(v\neq u)}[W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v)P_{[A]}(\epsilon_v,\alpha_v;t)-W_{[A]}{}^{\text{equil}}(\epsilon_v,\alpha_v/\epsilon_u,\alpha_u)P_{[A]}(\epsilon_u,\alpha_u;t)].\quad(14)$$

We proceed to discuss the relative magnitudes of $W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_u,\alpha_u')$ and $W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v)$, $(v\neq u)$ on the right side of Eq. (14). Let us suppose that not only is $V_{[B]}\gg V_{[A]}+V_{[AB]}{}^{\text{secular}}+V_{[AB]}{}^{\text{nonsecular}}$, but that in addition $V_{[A]}+V_{[AB]}{}^{\text{secular}}\gg V_{[AB]}{}^{\text{nonsecular}}$. Then from Eq. (I-61) we have

$$W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_u,\alpha_u')=\sum_{\beta_u,\beta_u'}W_{[A+B]}(\epsilon_u,\alpha_u;E-\epsilon_u,\beta_u/\epsilon_u,\alpha_u';E-\epsilon_u,\beta_u')/\mathfrak{N}_{[B]}(E-\epsilon_u)\gg W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v)$$
$$=\sum_{\beta_u,\beta_v}W_{[A+B]}(\epsilon_u,\alpha_u;E-\epsilon_u,\beta_u/\epsilon_v,\alpha_v;E-\epsilon_v,\beta_v)/\mathfrak{N}_{[B]}(E-\epsilon_v)\quad(v\neq u),\quad(15)$$

where the inequality follows since $V_{[A]}+V_{[AB]}{}^{\text{secular}}$ and $V_{[AB]}{}^{\text{nonsecular}}$ contribute, respectively, to $W_{[A+B]}(\epsilon_u,\alpha_u;E-\epsilon_u,\beta_u/\epsilon_u,\alpha_u';E-\epsilon_u,\beta_u')$ and $W_{[A+B]}(\epsilon_u,\alpha_u;E-\epsilon_u,\beta_u/\epsilon_v,\alpha_v;E-\epsilon_v,\beta_v)$, $(v\neq u)$ [see Eqs. (8), (4), and (3)]. Equation (15) shows that with arbitrary $P_{[A]}(\epsilon_u,\alpha_u;t_0)$, to begin with, the first term on the right side of Eq. (14) will dominate the second term. Under these circumstances the $P_{[A]}(\epsilon_u,\alpha_u;t)$ will first relax relatively rapidly toward the *quasi-equilibrium* values:

$$P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u;t)=P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u';t);\quad t-t_0\gtrsim T_{\text{quasi-equil }[A]},\quad(16)$$

and then, i.e., for $t-t_0\gtrsim T_{\text{quasi-equil }[A]}\gg T_{\text{quasi-equil }[B]}$, approach more slowly the ultimate and time-persistent equilibrium values given in Eq. (13). It is also worth mentioning that

$$\frac{d}{dt}\langle\epsilon\rangle_t\equiv\frac{d}{dt}\sum_{\epsilon_u,\alpha_u}\epsilon_u P_{[A]}(\epsilon_u,\alpha_u;t)=\sum_{\epsilon_u,\alpha_u}\epsilon_u\frac{dP_{[A]}(\epsilon_u,\alpha_u;t)}{dt}=\sum_{\epsilon_u,\alpha_u;\,\epsilon_v,\alpha_v(v\neq u)}(\epsilon_u-\epsilon_v)W_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u/\epsilon_v,\alpha_v)P_{[A]}(\epsilon_v,\alpha_v;t),$$

so that the transitions $[\epsilon_u,\alpha_u]\rightarrow[\epsilon_u,\alpha_u']$ associated with the action of $V_{[A]}+V_{[AB]}{}^{\text{secular}}$ do *not* contribute directly to the time rate of change of the average value of the energy of the system of interest $[A]$.

III. THE MASTER EQUATION FOR AN INDIVIDUAL PARTICLE OF THE SYSTEM OF INTEREST [A] AND TIME-DEPENDENT TEMPERATURES

Following the procedure of Eqs. (I-108)–(I-111), Eqs. (14) and (I-61) yield for the time rate of change of the occupation probability of the $[q]$th individual particle [see Eq. (5) for notation]:

$$\frac{d}{dt}P_{[q]}(u^{(q)};t)=\sum_{v^{(q)}}\{[W_{[q]}(u^{(q)}/v^{(q)};t)+w_{[q]}(u^{(q)}/v^{(q)};t)]P_{[q]}(v^{(q)};t)$$
$$-[W_{[q]}(v^{(q)}/u^{(q)};t)+w_{[q]}(v^{(q)}/u^{(q)};t)]P_{[q]}(u^{(q)};t)\},\quad(17)$$

where

$$P_{[q]}(u^{(q)};t)\equiv\sum_{\{u^{(i)}\}^{(q)}}P_{[A]}(\{u^{(i)}\};t)$$

and

$$\left\{\begin{matrix}W_{[q]}(u^{(q)}/v^{(q)};t)\\ w_{[q]}(u^{(q)}/v^{(q)};t)\end{matrix}\right\}=\sum_{\{u^{(i)}\}^{(q)},\{v^{(i)}\}^{(q)}}W_{[A]}{}^{\text{equil}}(\{u^{(i)}\}/\{v^{(i)}\})P_{[A]}(\{v^{(i)};t\})\left\{\begin{matrix}\delta(\epsilon_u,\epsilon_v)\\ [1-\delta(\epsilon_u,\epsilon_v)]\end{matrix}\right\}\Big/\sum_{\{v^{(i)}\}^{(q)}}P_{[A]}(\{v^{(i)}\};t)$$

$$=\sum_{\{u^{(i)}\}^{(q)},\{v^{(i)}\}^{(q)},\beta_u,\beta_v}\frac{W_{[A+B]}(\{u^{(i)}\};E-\epsilon_u,\beta_u/\{v^{(i)}\};E-\epsilon_v,\beta_v)}{\mathfrak{N}_{[B]}(E-\epsilon_v)}P_{[A]}(\{v^{(i)}\};t)\left\{\begin{matrix}\delta(\epsilon_u,\epsilon_v)\\ [1-\delta(\epsilon_u,\epsilon_v)]\end{matrix}\right\}\Big/$$

$$\sum_{\{v^{(i)}\}^{(q)}}P_{[A]}(\{v^{(i)}\};t)\quad(18)$$

and where $t-t_0\gtrsim T_{\text{quasi-equil }[B]}$. The individual particle transition probabilities $W_{[q]}(u^{(q)}/v^{(q)};t)$, $w_{[q]}(u^{(q)}/v^{(q)};t)$ are thus seen to be associated with transitions of the system of interest $[A]$ between states of equal energy and unequal energy, respectively, and arise from the interactions $V_{[A]}+V_{[AB]}{}^{\text{secular}}$ and $V_{[AB]}{}^{\text{nonsecular}}$, respectively. [See Eqs. (8), (4) and (3).] If the system of interest $[A]$ is, as a whole, *close to equilibrium*, we can write $P_{[A]}(\{v^{(i)}\};t)\cong P_{[A]}{}^{\text{equil}}(\{v^{(i)}\})$ so that combining Eqs. (18), and (13) or (I-60):

$$\frac{W_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})}{W_{[q]}{}^{\text{equil}}(v^{(q)}/u^{(q)})}=\frac{w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})}{w_{[q]}{}^{\text{equil}}(v^{(q)}/u^{(q)})}=\sum_{\{u^{(i)}\}^{(q)}}P_{[A]}{}^{\text{equil}}(\{u^{(i)}\})/\sum_{\{v^{(i)}\}^{(q)}}P_{[A]}{}^{\text{equil}}(\{v^{(i)}\})$$

$$=\sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u-\epsilon(u^{(q)}))P_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u)/\sum_{\epsilon_v}\mathfrak{N}_{[A]-[q]}(\epsilon_v-\epsilon(v^{(q)}))P_{[A]}{}^{\text{equil}}(\epsilon_v,\alpha_v)$$

$$=\sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u-\epsilon(u^{(q)}))\mathfrak{N}_{[B]}(E-\epsilon_u)/\sum_{\epsilon_v}\mathfrak{N}_{[A]-[q]}(\epsilon_v-\epsilon(v^{(q)}))\mathfrak{N}_{[B]}(E-\epsilon_v)$$

$$=e^{-\epsilon(u^{(q)})/\Theta[A]}e^{-[\epsilon(u^{(q)})]^2/2[\Theta[A]']^2}\cdots/e^{-\epsilon(v^{(q)})/\Theta[A]}e^{-[\epsilon(v^{(q)})]^2/2[\Theta[A]']^2}\cdots,\quad(19)$$

with

$$[\Theta_{[A]}]^{-1}\equiv\sum_{\epsilon_u}\left(\frac{d}{d\epsilon_u}\ln\mathfrak{N}_{[A]-[q]}(\epsilon_u)\right)\mathfrak{N}_{[A]-[q]}(\epsilon_u)\mathfrak{N}_{[B]}(E-\epsilon_u)\Big/\sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u)\mathfrak{N}_{[B]}(E-\epsilon_u)$$

$$\cong\frac{d}{d(\epsilon^{\dagger}(E))}\ln\mathfrak{N}_{[A]-[q]}(\epsilon^{\dagger}(E))\cong\frac{d}{d(\epsilon^{\dagger}(E))}\ln\mathfrak{N}_{[A]}(\epsilon^{\dagger}(E))\quad(20)$$

and

$$[\Theta_{[A]}']^{-2}\equiv\sum_{\epsilon_u}\left(\frac{d^2}{d\epsilon_u{}^2}\mathfrak{N}_{[A]-[q]}(\epsilon_u)\right)\mathfrak{N}_{[B]}(E-\epsilon_u)\Big/\sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u)\mathfrak{N}_{[B]}(E-\epsilon_u)+[\Theta_{[A]}]^{-2},\quad(21)$$

where, in Eq. (20), $\epsilon^{\dagger}(E)$ is the value of ϵ_u for which $\mathfrak{N}_{[A]-[q]}(\epsilon_u)\cdot\mathfrak{N}_{[B]}(E-\epsilon_u)$ has a (very sharp) maximum. An alternative form of $[\Theta_{[A]}]^{-1}$ can be obtained by differentiating:

$$\sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u)\mathfrak{N}_{[B]}(E-\epsilon_u)=\sum_{\eta_u}\mathfrak{N}_{[A]-[q]}(E-\eta_u)\mathfrak{N}_{[B]}(\eta_u)$$

with respect to E; we find:

$$[\Theta_{[A]}]^{-1}=\sum_{\epsilon_u}\left(\frac{\partial}{\partial E}\ln\mathfrak{N}_{[B]}(E-\epsilon_u)\right)\mathfrak{N}_{[A]-[q]}(\epsilon_u)\mathfrak{N}_{[B]}(E-\epsilon_u)\Big/\sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u)\mathfrak{N}_{[B]}(E-\epsilon_u)$$

$$\cong\frac{\partial}{\partial E}\ln\mathfrak{N}_{[B]}(E-\epsilon^{\dagger}(E)).\quad(22)$$

Since, in addition [see Eq. (13) or Eq. (I-60)]

$$\langle\epsilon\rangle^{\text{equil}}\cong\langle\epsilon-\epsilon^{(q)}\rangle^{\text{equil}}=\sum_{\{u^{(i)}\}^{(q)}}[\epsilon_u-\epsilon(u^{(q)})]P_{[A]-[q]}{}^{\text{equil}}(\{u^{(i)}\}^{(q)})$$

$$=\sum_{\epsilon_u}[\epsilon_u-\epsilon(u^{(q)})]\mathfrak{N}_{[A]-[q]}(\epsilon_u-\epsilon(u^{(q)}))\mathfrak{N}_{[B]}(E-\epsilon_u-\epsilon(u^{(q)}))/\sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u-\epsilon(u^{(q)}))\mathfrak{N}_{[B]}(E-\epsilon_u-\epsilon(u^{(q)}))$$

$$\cong\epsilon^{\dagger}(E),\quad(23)$$

we have from Eqs. (22) and (23)

$$[\Theta_{[A]}]^{-1} \cong \frac{\partial}{\partial E} \ln \mathfrak{N}_{[B]}(E-\langle\epsilon\rangle^{\text{equil}}). \tag{24}$$

Similarly, we obtain

$$\begin{aligned}[\Theta_{[A]}']^{-2} &\cong -\frac{\partial^2}{\partial E^2} \ln \mathfrak{N}_{[B]}(E-\langle\epsilon\rangle^{\text{equil}}) \\ &\cong -\frac{\partial}{\partial E}[\Theta_{[A]}(E)]^{-1} \approx [\Theta_{[A]}(E)]^{-1}/E,\end{aligned} \tag{25}$$

so that, as long as $[A]$ and $[B]$ each contain a large number of individual particles, we can replace $e^{-[\epsilon(u^{(q)})]^2/2[\Theta_{[A]}']^2} \approx e^{-[\epsilon(u^{(q)})/\Theta_{[A]}][\epsilon(u^{(q)})/2E]}$ by unity and write on the basis of Eqs. (19) and (17)

$$\begin{gathered}\frac{W_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})}{W_{[q]}{}^{\text{equil}}(v^{(q)}/u^{(q)})} = \frac{w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})}{w_{[q]}{}^{\text{equil}}(v^{(q)}/u^{(q)})} = \frac{e^{-\epsilon(u^{(q)})/\Theta_{[A]}}}{e^{-\epsilon(v^{(q)})/\Theta_{[A]}}}, \\ P_{[q]}{}^{\text{equil}}(u^{(q)}) = e^{-\epsilon(u^{(q)})/\Theta_{[A]}} \Big/ \sum_{u^{(q)}} e^{-\epsilon(u^{(q)})/\Theta_{[A]}}.\end{gathered} \tag{26}$$

It is to be emphasized that Eq. (24) for $\Theta_{[A]}$ is identical with Eq. (I-63) for $\Theta \equiv kT$ provided that $\langle\epsilon\rangle^{\text{equil}} \ll E \approx \langle\eta\rangle^{\text{equil}}$, i.e., provided that $[A] \ll [B]$; thus Eq. (26) and in fact all of the results in the present paper, derived for the case $[A] \approx [B]$ (i.e., $\langle\epsilon\rangle^{\text{equil}} \approx E \approx \langle\eta\rangle^{\text{equil}}$), become the corresponding results for the case $[A] \ll [B]$ if $\Theta_{[A]}$ is replaced by Θ. It may also be mentioned that $\Theta_{[B]}$, defined, e.g., as in Eq. (22) but with the roles of $[A]$, $[B]$ interchanged, can be shown to be equal to $\Theta_{[A]}$; this result is, of course, necessary for a consistent treatment of equilibrium between $[A]$ and $[B]$.

As a particular application of Eqs. (17), (18) we deduce the equation for the time rate of change of the average energy of the $[q]$th individual particle, $\langle\epsilon_{[q]}\rangle_t$. Thus,

$$\begin{aligned}\frac{d}{dt}\langle\epsilon_{[q]}\rangle_t &\equiv \frac{d}{dt}\sum_{u^{(q)}} \epsilon(u^{(q)}) P_{[q]}(u^{(q)};t) = \sum_{u^{(q)}} \epsilon(u^{(q)}) \frac{dP_{[q]}(u^{(q)};t)}{dt} \\ &= \sum_{u^{(q)},v^{(q)}} \epsilon(u^{(q)})[W_{[q]}(u^{(q)}/v^{(q)};t)P_{[q]}(v^{(q)};t) - W_{[q]}(v^{(q)}/u^{(q)};t)P_{[q]}(u^{(q)};t)] \\ &\quad + \sum_{u^{(q)},v^{(q)}} \epsilon(u^{(q)})[w_{[q]}(u^{(q)}/v^{(q)};t)P_{[q]}(v^{(q)};t) - w_{[q]}(v^{(q)}/u^{(q)};t)P_{[q]}(u^{(q)};t)] \\ &= \sum_{\{u^{(i)}\},\{v^{(i)}\}} (\epsilon_u/\mathfrak{N}_{[A]})[W_{[A]}{}^{\text{equil}}(\{u^{(i)}\}/\{v^{(i)}\})P_{[A]}(\{v^{(i)}\};t) - W_{[A]}{}^{\text{equil}}(\{v^{(i)}\}/\{u^{(i)}\})P_{[A]}(\{u^{(i)}\};t)]\delta(\epsilon_u,\epsilon_v) \\ &\qquad + \sum_{u^{(q)},v^{(q)}} [\epsilon(u^{(q)}) - \epsilon(v^{(q)})][w_{[q]}(u^{(q)}/v^{(q)};t)P_{[q]}(v^{(q)};t)],\end{aligned} \tag{27}$$

where we have used, in the first term on the right side, the identity of the individual particles and the effective additivity of their energies to form ϵ_u. This first term on the right side is now seen to vanish [because the $\delta(\epsilon_u,\epsilon_v)$ only admits contributions to $\sum_{\{u^{(i)}\},\{v^{(i)}\}}\cdots$ with $\epsilon_u = \epsilon_v$] and we obtain

$$\begin{aligned}\frac{d}{dt}\langle\epsilon_{[q]}\rangle_t &= \sum_{u^{(q)},v^{(q)}} [\epsilon(u^{(q)}) - \epsilon(v^{(q)})][w_{[q]}(u^{(q)}/v^{(q)};t)P_{[q]}(v^{(q)};t)] \\ &= \tfrac{1}{2} \sum_{u^{(q)},v^{(q)}} [\epsilon(u^{(q)}) - \epsilon(v^{(q)})][w_{[q]}(u^{(q)}/v^{(q)};t)P_{[q]}(v^{(q)};t) - w_{[q]}(v^{(q)}/u^{(q)};t)P_{[q]}(u^{(q)};t],\end{aligned} \tag{28}$$

which is to be compared with the expression derived above for $(d/dt)\langle\epsilon\rangle_t$ in that again only transitions of the system of interest between states of unequal energy contribute to $(d/dt)\langle\epsilon_{[q]}\rangle_t$.

We now consider the values of $W_{[q]}(u^{(q)}/v^{(q)};t)$ in the *quasi-equilibrium* statistical configuration for $[A]$; in this statistical configuration $P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u;t) = P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u';t)$ for all α_u, α_u'; $t-t_0 \gtrsim T_{\text{quasi-equil }[A]}$

[Eqs. (14)–(16)]. From Eqs. (18) and (16) we then have

$$\frac{W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)}{W_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)}/u^{(q)};t)} = \sum_{\{u^{(i)}\}(q)} P_{[A]}{}^{\text{quasi-equil }[A]}(\{u^{(i)}\};t)\Big/ \sum_{\{v^{(i)}\}(q)} P_{[A]}{}^{\text{quasi-equil }[A]}(\{v^{(i)}\};t)$$
$$=\sum_{\epsilon_u} \mathfrak{N}_{[A]-[q]}(\epsilon_u-\epsilon(u^{(q)}))P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u;t)\Big/\sum_{\epsilon_u} \mathfrak{N}_{[A]-[q]}(\epsilon_v-\epsilon(v^{(q)}))P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_v,\alpha_v;t), \quad (29)$$

so that, by an argument similar to that in Eqs. (19)–(26), we have

$$W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)/W_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)}/u^{(q)};t)=e^{-\epsilon(u^{(q)})/\Theta_{[A]}(t)}/e^{-\epsilon(v^{(q)})/\Theta_{[A]}(t)}, \quad (30)$$

with a *time-dependent* temperature $\Theta_{[A]}(t)$ defined by

$$[\Theta_{[A]}(t)]^{-1}\equiv\sum_{\epsilon_u}\left(\frac{d}{d\epsilon_u}\ln\mathfrak{N}_{[A]-[q]}(\epsilon_u)\right)\mathfrak{N}_{[A]-[q]}(\epsilon_u)P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u;t)\Big/ \sum_{\epsilon_u}\mathfrak{N}_{[A]-[q]}(\epsilon_u)P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u;t). \quad (31)$$

Equations (31) and (20) show that as $P_{[A]}{}^{\text{quasi-equil }[A]}(\epsilon_u,\alpha_u;t)\rightarrow P_{[A]}{}^{\text{equil}}(\epsilon_u,\alpha_u)=\mathfrak{N}_{[B]}(E-\epsilon_u)/\mathfrak{N}$ [Eq. (I-60)], $\Theta_{[A]}(t)\rightarrow\Theta_{[A]}$.

We proceed to treat Eqs. (17) and (18) for the evolution in time of the $P_{[q]}(u^{(q)};t)$ for $t-t_0\gtrsim T_{\text{quasi-equil }[A]}\gg T_{\text{quasi-equil }[B]}$ in a *self-consistent approximation* where we replace $W_{[q]}(u^{(q)}/v^{(q)};t)$ and $w_{[q]}(u^{(q)}/v^{(q)};t)$ by $W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)$ and $w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)};t)$. We then have from Eqs. (17), (18), (30), and (26):

$$\frac{d}{dt}P_{[q]}(u^{(q)};t)=\sum_{v^{(q)}} W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)\left\{P_{[q]}(v^{(q)};t)-\exp\left[\frac{-[\epsilon(v^{(q)})-\epsilon(u^{(q)})]}{\Theta_{[A]}(t)}\right]P_{[q]}(u^{(q)};t)\right\}$$
$$+\sum_{v^{(q)}} w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})\left\{P_{[q]}(v^{(q)};t)-\exp\left[\frac{-[\epsilon(v^{(q)})-\epsilon(u^{(q)})]}{\Theta_{[A]}}\right]P_{[q]}(u^{(q)};t)\right\}. \quad (32)$$

The replacement used is suggested by the fact that Eq. (18) shows that the transition probabilities $W_{[q]}(u^{(q)}/v^{(q)};t)$ and $w_{[q]}(u^{(q)}/v^{(q)};t)$, in general, depend on time much more slowly than $P_{[A]}(\{v^{(i)}\};t)$ and $P_{[q]}(v^{(q)};t)\equiv\sum_{\{v^{(i)}\}(q)} P_{[A]}(\{v^{(i)}\};t)$, and by the fact that $W_{[q]}(u^{(q)}/v^{(q)};t)$ and $w_{[q]}(u^{(q)}/v^{(q)};t)$ tend to establish quasi-equilibrium for $[A]$ and equilibrium between $[A]$ and $[B]$, respectively. Supposing further that $V_{[A]}+V_{[AB]}{}^{\text{secular}}\gg V_{[AB]}{}^{\text{nonsecular}}$, we have [see Eqs. (18), (15), (8), (4), and (3)]:

$$W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)\gg w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)}), \quad (33)$$

so that, setting

$$P_{[q]}(u^{(q)};t)\equiv P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)+D_{[q]}(u^{(q)};t),$$
$$P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)\equiv e^{-\epsilon(u^{(q)})/\Theta_{[A]}(t)}\Big/\sum_{u^{(q)}} e^{-\epsilon(u^{(q)})/\Theta_{[A]}(t)}, \quad (34)$$
$$D_{[q]}(u^{(q)};t)\ll P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t);\quad t-t_0\gtrsim T_{\text{quasi-equil }[A]},$$

and substituting Eq. (34) into Eq. (32) we get

$$\frac{d}{dt}P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t) =\left\{\frac{d}{d(1/\Theta_{[A]}(t))}[P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)]\right\}\frac{d}{dt}\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right)$$
$$\cong\sum_{v^{(q)}} W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)\{D_{[q]}(v^{(q)};t)-e^{-[\epsilon(v^{(q)})-\epsilon(u^{(q)})]/\Theta_{[A]}(t)}D_{[q]}(u^{(q)};t)\}$$
$$+\sum_{v^{(q)}} w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})\{P_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)};t)-e^{-[\epsilon(v^{(q)})-\epsilon(u^{(q)})]/\Theta_{[A]}}P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)\};$$
$$t-t_0\gtrsim T_{\text{quasi-equil }[A]}. \quad (35)$$

Equation (35) determines the relatively small terms $D_{[q]}(u^{(q)};t)$ if the time-dependent temperature $\Theta_{[A]}(t)$ is known. To find this $\Theta_{[A]}(t)$ we substitute $P_{[q]}(u^{(q)};t)\cong P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)$ [Eq. (34)] and $w_{[q]}(u^{(q)}/v^{(q)};t)\cong w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})$ [Eq. (32) ff] into Eq. (28) for

$$\frac{d}{dt}\langle\epsilon_{[q]}\rangle_t=\sum_{u^{(q)}}\epsilon(u^{(q)})\frac{dP_{[q]}}{dt}(u^{(q)};t)$$

and obtain

$$\frac{d}{dt}\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right)\cong\frac{\begin{array}{l}-\frac{1}{2}\sum_{u^{(q)},v^{(q)}}[\epsilon(u^{(q)})-\epsilon(v^{(q)})]w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})\\ \qquad\times\{P_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)};t)-e^{-[\epsilon(v^{(q)})-\epsilon(u^{(q)})]/\Theta[A]}P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)\}\end{array}}{\langle(\epsilon_{[q]})^2\rangle_t{}^{\text{quasi-equil }[A]}-(\langle\epsilon_{[q]}\rangle_t{}^{\text{quasi-equil }[A]})^2};$$

$$t-t_0\gtrsim T_{\text{quasi-equil }[A]},\tag{36}$$

with

$$\langle(\epsilon_{[q]})^n\rangle_t{}^{\text{quasi-equil }[A]}\equiv\sum_{u^{(q)}}[\epsilon(u^{(q)})]^nP_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t).\tag{37}$$

Equations (36) and (37) yield $\Theta_{[A]}(t)$ which, apart from the $D_{[q]}(u^{(q)};t)$, determines the evolution in time of the "Boltzmann-like" $P_{[q]}(u^{(q)};t)$ of Eq. (34)—it will be noted that on the basis of Eqs. (35)–(37)

$$D_{[q]}(u^{(q)};t)\approx[w^{\text{equil}}(u^{(q)}/v^{(q)})/W^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)](P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)-P_{[q]}{}^{\text{equil}}(u^{(q)}))$$

and so $D_{[q]}(u^{(q)};t)\ll 1$ [Eq. (33)]. Two specially simple cases of Eqs. (36) and (37) may be mentioned[8]

α: $\Theta_{[A]}(t), \Theta_{[A]}\gg\epsilon(u^{(q)})$ for all important states $u^{(q)}$

$$\frac{d}{dt}\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right)\cong-\tau_\alpha{}^{-1}\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right),\tag{38}$$

$$\tau_\alpha{}^{-1}\equiv\tfrac{1}{2}\sum_{u^{(q)},v^{(q)}}[\epsilon(u^{(q)})-\epsilon(v^{(q)})]^2w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})/\{\sum_{u^{(q)}}\epsilon(u^{(q)})^2-[\sum_{u^{(q)}}\epsilon(u^{(q)})]^2/(\sum_{u^{(q)}}1)\},\tag{39}$$

$$\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right)=\left(\frac{1}{\Theta_{[A]}(t^*)}-\frac{1}{\Theta_{[A]}}\right)e^{-(t-t^*)/\tau_\alpha};\quad t-t_0\gtrsim t^*-t_0\equiv T_{\text{quasi-equil }[A]}.\tag{40}$$

β: $\epsilon(u^{(q)})(1/\Theta_{[A]}(t)-1/\Theta_{[A]})\ll 1$ for all important states $u^{(q)}$ and all t considered

$$\frac{d}{dt}\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right)\cong-\tau_\beta{}^{-1}\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right),\tag{41}$$

$$\tau_\beta{}^{-1}\equiv\tfrac{1}{2}\sum_{u^{(q)},v^{(q)}}[\epsilon(u^{(q)})-\epsilon(v^{(q)})]^2w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})P_{[q]}{}^{\text{equil}}(v^{(q)})/\{\sum_{u^{(q)}}[\epsilon(u^{(q)})]^2P_{[q]}{}^{\text{equil}}(u^{(q)})-[\sum_{u^{(q)}}\epsilon(u^{(q)})P_{[q]}{}^{\text{equil}}(u^{(q)})]^2\},\tag{42}$$

$$\left(\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right)=\left(\frac{1}{\Theta_{[A]}(t^*)}-\frac{1}{\Theta_{[A]}}\right)e^{-(t-t^*)/\tau_\beta};\quad t-t_0\gtrsim t^*-t_0\equiv T_{\text{quasi-equil }[A]}.\tag{43}$$

Equations (40), (43), (34), and (35) determine the evolution of $P_{[q]}(u^{(q)};t)$ toward its equilibrium value of $P_{[q]}{}^{\text{equil}}(u^{(q)})$ given in Eq. (26) (see also Appendix A). It is also interesting to mention that for

$$\Theta_{[A]}\ll\epsilon(1^{(q)})-\epsilon(0^{(q)});\quad\epsilon(0^{(q)})<\epsilon(1^{(q)})<\epsilon(2^{(q)})<\cdots,\tag{44}$$

Eq. (42) reduces to

$$\tau_\beta{}^{-1}=\frac{w_{[q]}{}^{\text{equil}}(0^{(q)}/1^{(q)})}{1-\exp\{-[\epsilon(1^{(q)})-\epsilon(0^{(q)})]/\Theta_{[A]}\}},\tag{45}$$

[8] The result in Eqs. (38)–(40) was first obtained in the special case of magnetic resonance ($\Theta_{[A]}(t)$ is then the time-dependent spin temperature $\Theta_{[S]}(t)$) by L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

so that the rate of relaxation of $\Theta_{[A]}(t)$ toward $\Theta_{[A]}$ becomes independent of $\Theta_{[A]}$ for very low $\Theta_{[A]}$ provided that $w_{[q]}{}^{\text{equil}}(0^{(q)}/1^{(q)})$ is itself independent of $\Theta_{[A]}$. This is expected on the basis of physical considerations in many instances—e.g., when the $[q]$th individual particle of the system of interest $[A]$ is the $[q]$th nuclear spin with ground, first, $\cdots$, excited states: $\psi_{[q]}(0^{(q)})$, $\psi_{[q]}(1^{(q)})$, $\cdots\{\epsilon(0^{(q)})=-\mu H_0,\ \epsilon(1^{(q)})=-\mu[(I-1)/I]H_0,\ \cdots\}$ and when the relaxation transition $\psi_{[q]}(1^{(q)})\rightarrow\psi_{[q]}(0^{(q)})$ involves the creation of a phonon in the surroundings $[B]$.

We next consider situations where $V_{[A]}+V_{[AB]}{}^{\text{secular}}\ll V_{[AB]}{}^{\text{nonsecular}}$ so that $W_{[q]}(u^{(q)}/v^{(q)};t)\ll w_{[q]}(u^{(q)}/v^{(q)};t)$ in Eqs. (17), (18), and (32). In this case Eq. (32) for the $P_{[q]}(u^{(q)};t)$ becomes to a sufficient approximation

$$\frac{d}{dt}P_{[q]}(u^{(q)};t)=\sum_{v^{(q)}}w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})\left\{P_{[q]}(v^{(q)};t)-\exp\left[-\frac{\epsilon(v^{(q)})-\epsilon(u^{(q)})}{\Theta_{[A]}}\right]P_{[q]}(u^{(q)};t)\right\},\tag{46}$$

and its solution is given in Eqs. (I-130)–(I-132) in the general form

$$P_{[q]}(u^{(q)};t)=P_{[q]}{}^{\text{equil}}(u^{(q)})+\textstyle\sum_\nu K_\nu(u^{(q)})e^{-\omega_\nu(t-t_0)},\tag{47}$$

with the ω_1, ω_2, $\cdots$ playing the role of $[w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})-\text{dependent}]$ relaxation rates and the $K_\nu(u^{(q)})$ depending on $P_{[q]}(u^{(q)};t_0)$ as well as on $w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})$. This case is discussed in detail in I [see Eqs. (I-110)–(I-145)].

IV. TIME-DEPENDENT SPIN TEMPERATURES IN MAGNETIC RESONANCE

We proceed to apply the general theory of the preceding three sections to the concept of a time-dependent spin temperature $\Theta_{[S]}(t)\equiv\Theta_{[A]}(t)$ in magnetic resonance. It is now fully appreciated[9] that the supposition that the spin system of interest $[A]$ returns to equilibrium along a succession of Boltzmann distributions, each described by an appropriate $\Theta_{[A]}(t)$, is not just a convenient artifice to find an approximate solution of the master equation for $[A]$ but is in many circumstances an accurate description of the corresponding relaxation process [see the general discussion in Eqs. (32)–(45) above].

The spin system of interest $[A]$ will be properly characterized for times $t-t_0\gtrsim T_{\text{quasi-equil }[A]}$ by a time-dependent spin temperature $\Theta_{[A]}(t)$ if $W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)\gg w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})$ [Eqs. (33)–(45)]; in general no such characterization will be possible if the inequality is reversed. An example of how one calculates $W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)$ is worked out in Appendix B where it is shown that $W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)$ arises from the "flip-flop" terms of the secular part of the magnetic dipole-dipole interaction; from Eq. (B1) these "flip-flop" terms are

$$\begin{aligned}
&V_{[A]}\equiv V_{\text{dip-dip}}{}^{\text{secular flip-flop}}=\tfrac{1}{4}\sum_{f,g}A_{fg}[I_{[f]+}I_{[g]-}+I_{[f]-}I_{[g]+}],\\
&A_{fg}\equiv(-\tfrac{1}{2}\hbar^2\gamma^2/r_{fg}{}^3)(1-3\cos^2\Theta_{fg}),\\
&\mathbf{r}_f-\mathbf{r}_g\equiv(r_{fg},\Theta_{fg},\phi_{fg}),\\
&\mathbf{r}_f\equiv\mathbf{R}_f+\boldsymbol{\xi}_f\cong\mathbf{R}_f\ \text{(rigid lattice)},
\end{aligned}\tag{48}$$

whence Eqs. (B6), (B7) yield, with $u^{(q)}=m_q\doteq I_{[q]z}$, $\epsilon(u^{(q)})=-\hbar\gamma H_0m_q$,

$$\begin{aligned}
W_{[q]}{}^{\text{quasi-equil }[A]}(m_q-1/m_q;t)&=e^{-\hbar\gamma H_0/\Theta_{[A]}(t)}W_{[q]}{}^{\text{quasi-equil }[A]}(m_q/m_q-1;t)\\
&=(I-m_q+1)(I+m_q)W_{[q]}(t)/\{\sum_{m_q}e^{m_q\hbar\gamma H_0/\Theta_{[A]}(t)}\},\\
W_{[q]}(t)&\equiv\frac{\pi}{8}(\gamma H_0)\sum_p(A_{qp}/\hbar\gamma H_0)^2[I(I+1)-\langle m_p{}^2\rangle_t{}^{\text{quasi-equil }[A]}-\langle m_p\rangle_t{}^{\text{quasi-equil }[A]}],
\end{aligned}\tag{49}$$

and a spin temperature $\Theta_{[A]}(t)$ exists if this $W_{[q]}{}^{\text{quasi-equil }[A]}(m_q-1/m_q;t)\gg w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$. In a nuclear spin $I=1/2$ insulating crystal with a normal concentration of paramagnetic impurities $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$ arises ultimately from $V_{[AB]}{}^{\text{nonsecular}}=\{V_{\text{dip-dip}}$ of nuclear spin-impurity electronic spin$\}$ and this in general gives $w_{[q]}(m_q-1/m_q)\ll W_{[q]}{}^{\text{quasi-equil }[A]}(m_q-1/m_q)$. In a normally impure crystal with nuclear spin $I>1/2$, e.g., NaCl with $I(\text{Na}^{23})=I(\text{Cl}^{35})=3/2$, $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$ is however dominated by $V_{[AB]}{}^{\text{nonsecular}}=V_{\text{quad.}}{}^{\text{nonsecular}}$ of Eq. (I-125) [the corresponding $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$ are then given by Eqs. (I-126)–(I-129)]; in this case it is not difficult to set up situations where $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$ is $\gg$ as well as $\ll W_{[q]}{}^{\text{quasi-equil }[A]}(m_q-1/m_q;t)$ (see below). As an illustration we shall in fact consider the case of NaCl and first suppose that the $W_{[q]}{}^{\text{quasi-equil }[A]}(m_q-1/m_q;t)$ of Eq. (49) is much larger than the $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$ of Eqs. (I-126)–(I-129).

[9] A. Abragam and W. J. Proctor, Phys. Rev. **109**, 1441 (1958). See also R. T. Schumacher, *ibid.* **112**, 837 (1958).

Then a time-dependent spin temperature $\Theta_{[A]}(t)$ exists and is determined by Eqs. (36)–(40) and the

$$P_{[q]}(m_q;t)\cong P_{[q]}{}^{\text{quasi-equil }[A]}(m_q;t)=e^{m_q\hbar\gamma H_0/\Theta_{[A]}(t)}/\{\sum_{m_q} e^{m_q\hbar\gamma H_0/\Theta_{[A]}(t)}\},$$

indeed, return to equilibrium along a succession of Boltzmann distributions. The longitudinal magnetization

$$\langle\mu\rangle_t=\langle(\hbar\gamma/V_{[A]})I_z\rangle_t=\sum_{m_q} P_{[q]}(m_q;t)\frac{N_{[A]}}{V_{[A]}}\hbar\gamma m_q;$$

[Eq. (I-133)] is then given by[10]

$$\frac{\langle\mu\rangle_t-\langle\mu\rangle^{\text{equil}}}{\langle\mu\rangle^{\text{equil}}}=-2\exp[-(24/5)(w'+4w'')(t-t^*)], \tag{50}$$

where w' and w'' are quantities defined in Eqs. (I-126)–(I-129) as proportional to $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$ and $w_{[q]}{}^{\text{equil}}(m_q-2/m_q)$, respectively,[11] and the conditions at time t^* correspond to those existing immediately after a 180° pulse, i.e., $\langle\mu\rangle_{t=t^*}=-\langle\mu\rangle^{\text{equil}}$. On the other hand, if $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$ is much larger than $W_{[q]}{}^{\text{quasi-equil }[A]}(m_q-1/m_q;t)$, no $\Theta_{[A]}(t)$ can be defined and Eqs. (46) and (47) must be used to obtain the $P_{[q]}(m_q;t)$. A long but straightforward calculation (see also, Appendix B of I) then yields these $P_{[q]}(m_q;t)$ and the corresponding $\langle\mu\rangle_t$ is

$$\frac{\langle\mu\rangle_t-\langle\mu\rangle^{\text{equil}}}{\langle\mu\rangle^{\text{equil}}}=-2\{(1/5)\exp[-24w'(t-t^*)]+(4/5)\exp[-24w''(t-t^*)]\}. \tag{51}$$

We now remark that the $\langle\mu\rangle_t$ of Eq. (50) and the $\langle\mu\rangle_t$ of Eq. (51) are identical if $w'=w''$ so that an experimental distinction between the case where a time-dependent spin temperature is present and one where no time-dependent spin temperature exists depends on the magnitude of the parameter $(w'-w'')/w'$. This parameter can be obtained from the explicit values of $w_{[q]}{}^{\text{equil}}(m_q-1/m_q)$, $w_{[q]}{}^{\text{equil}}(m_q-2/m_q)$ (and hence of w', w'') given by Van Kranendonk[12] and is

$$\frac{w'-w''}{w'}=\frac{78-390\alpha^2}{723-312\alpha^2}, \tag{52}$$
$$\alpha^2\equiv\alpha_1{}^2\alpha_2{}^2+\alpha_1{}^2\alpha_3{}^2+\alpha_2{}^2\alpha_3{}^2,$$

where α_1, α_2, α_3 are the direction cosines between the magnetic field $\mathbf{H}_0$ and the three cubic axes, and $0\leqq\alpha^2\leqq 1/3$, so that $(w'-w'')/w'\cong 1/10$. Thus, the difference between the $\langle\mu\rangle_t$ of Eq. (50) and the $\langle\mu\rangle_t$ of Eq. (51), while small, should be measurable. A proposed experiment in NaCl designed to set up the conditions $W_{[q]}{}^{\text{quasi-equil }[A]}\gg w_{[q]}{}^{\text{equil}}$ and $W_{[q]}{}^{\text{quasi-equil }[A]}\ll w_{[q]}{}^{\text{equil}}$ and so establish alternately the $\langle\mu\rangle_t$ of Eq. (50) and the $\langle\mu\rangle_t$ of Eq. (51) may be attempted as follows.

We first study the Na resonance and produce the condition where $W_{[q]}{}^{\text{quasi-equil }[A]}\ll w_{[q]}{}^{\text{equil}}$ [$\Theta_{[A]}(t)\equiv\Theta_{[\text{Na}]}(t)$ does not exist; Eq. (51) applies] by reducing the $A_{qp}(\text{Na}-\text{Na})$ of Eqs. (49), (48) to very small effective values. This reduction is accomplished by rotating the NaCl crystal rapidly about one of its cubic axes, the axis of rotation being set at an angle $\alpha_1=1/\sqrt{3}$ relative to the magnetic field.[13] On the other hand, the condition $W_{[A]}{}^{\text{quasi-equil }[A]}\gg w_{[q]}{}^{\text{equil}}$ [$\Theta_{[\text{Na}]}(t)$ exists; Eq. (50) applies] holds normally in the nonrotating crystal which, for simplicity, can be oriented with $\alpha_1=\alpha_2=\alpha_3=1/\sqrt{3}$.

A second method to pass from one of the two cases of interest to the other involves the study of the Cl resonance. Since $\gamma(\text{Na})\gg\gamma(\text{Cl})$ the local magnetic field seen by a typical Cl nucleus is essentially due to the various Na nuclei, and this local field varies rather rapidly from one Cl site to another.[14] As a result the secular character of $\frac{1}{4}\sum_{f,g}A_{fg}(\text{Cl}-\text{Cl})[I_{[f]+}I_{[g]-}+I_{[f]-}I_{[g]+}]$ is destroyed [see Eqs. (48) and (49)], $W_{[q]}{}^{\text{quasi-equil }[A]}$ becomes

[10] The expression in Eq. (50) was first obtained by R. S. Meiher, Phys. Rev. Letters, 4, 57 (1960).

[11] On the basis of Eqs. (34)–(45) it should be emphasized again that the time dependence of the $\Theta_{[A]}(t)$ and so of the $P_{[q]}(m_q;t)\cong P_{[q]}{}^{\text{quasi-equil }[A]}(m_q;t)$ is given solely by the $w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})$ even in this case where $w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})\ll W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)$.

[12] J. Van Kranendonk, Physica **20**, 781 (1954).

[13] See for example J. Dreitlein and H. Kessemeir, Phys. Rev. **123**, 835 (1961); I. J. Lowe, Phys. Rev. Letters **2**, 285 (1959); E. Andrew and R. Newing, Proc. Phys. Soc. (London) **72**, 959 (1958).

[14] A similar idea has been successfully exploited by R. V. Pound who measured the change in $T_1(\text{Li})$ ($\langle\mu\rangle_t-\langle\mu\rangle^{\text{equil}}\sim e^{-(t-t_0)/T_1}$) for a LiF crystal [$\gamma(\text{Li})\ll\gamma(\text{F})$] as a function of α^2. In this case $T_1(\text{Li})$ is dominated by nuclear spin diffusion to paramagnetic impurities. See R. V. Pound, J. Phys. Chem. **57**, 743 (1953), and A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 386.

$\ll w_{[q]}{}^{\text{equil}}$ and $\Theta_{[\text{Cl}]}(t)$ does not exist [Eq. (51) applies]. If contrariwise, the local magnetic field due to the various Na nuclei is averaged out by application of an intense rf magnetic field at the Na resonance frequency, $V_{\text{dip-dip}}{}^{\text{secular flip-flop}}(\text{Cl}-\text{Cl})$ is returned to its normal value, $W_{[q]}{}^{\text{quasi-equil }[A]}$ is again $\gg w_{[q]}{}^{\text{equil}}$ and a $\Theta_{[\text{Cl}]}(t)$ is present [Eq. (50) applies].

We now proceed to a discussion of the transverse magnetization $\langle\mu'\rangle_t=\langle(\hbar\gamma/V_{[A]})I_x\rangle_t$ from the point of view of the existence of a time-dependent spin temperature in a frame rotating with angular velocity γH_0 relative to the laboratory frame.[15] Here the theory of Eqs. (7)–(47) cannot in general be immediately used, since as shown in I [Eqs. (I-162)–(I-190)], a master equation for the time evolution of the appropriate statistical configuration cannot in this case always be defined.

To treat the problem we consider instead the transverse magnetization $\langle\mu'\rangle_t$ following a 90° pulse and assume further that the rf magnetic field associated with the pulse, $\mathbf{H}_1(t)$, is not removed at time t_0 but rather has a $(-90°)$ phase shift introduced into it. We then have

$$\begin{aligned}
\mathbf{H}_1(t)&=-H_1\{\sin[\omega_L(t-t_0)]\hat{x}+\cos[\omega_L(t-t_0)]\hat{y}\},\quad t_0-\frac{\pi/2}{\omega_1}\leqq t\leqq t_0;\\
\mathbf{H}_1(t)&=-H_1\{\sin[\omega_L(t-t_0)-\pi/2]\hat{x}+\cos[\omega_L(t-t_0)-\pi/2]\hat{y}\},\quad t_0<t;\\
\omega_L&\equiv\gamma H_0;\quad \omega_1\equiv\gamma H_1.
\end{aligned}\tag{53}$$

In addition, Eqs. (I-146) and (I-147) yield

$$\begin{aligned}
\langle\mu'\rangle_t&=\langle(\hbar\gamma/V_{[A]})I_x\rangle_t=(\hbar\gamma/V_{[A]})\,\text{Trace}\{\rho(t)I_x\}\\
&=(\hbar\gamma/V_{[A]})\,\text{Trace}\{\rho_{\text{rot}}(t)I_{x:\text{rot}}(t)\},
\end{aligned}\tag{54}$$

where

$$\begin{aligned}
\rho(t)&=\rho(t_0)+(i/\hbar)\int_{t_0}^{t}[\rho(t'),\mathcal{H}(t')]dt',\\
\mathcal{H}(t)&=\mathcal{H}_{[A]}{}^{(0)}+\mathcal{H}_{[B]}{}^{(0)}+V+\mathcal{H}_{\text{rf}}(t)\equiv\mathcal{H}^{(0)}+V^{\text{secular}}+V^{\text{nonsecular}}+\mathcal{H}_{\text{rf}}(t),\\
\mathcal{H}_{[A]}{}^{(0)}&\equiv-\hbar\omega_L I_z;\quad \mathcal{H}_{\text{rf}}(t)\equiv-\hbar\omega_1\mathbf{I}\cdot\hat{H}_1(t),\\
\rho(t_0)&=\frac{e^{\hbar\omega_L I_x/\Theta_{[A]}}e^{-\mathcal{H}_{[B]}{}^{(0)}/\Theta_{[B]}}}{\text{Trace}\{e^{\hbar\omega_L I_x/\Theta_{[A]}}e^{-\mathcal{H}_{[B]}{}^{(0)}/\Theta_{[B]}}\}};\quad \Theta_{[A]}=\Theta_{[B]},\\
\rho_{\text{rot}}(t)&\equiv e^{(i/\hbar)(t-t_0)\mathcal{H}_{[A]}{}^{(0)}}\rho(t)e^{-(i/\hbar)(t-t_0)\mathcal{H}_{[A]}{}^{(0)}}\\
&=e^{-i\omega_L(t-t_0)I_z}\rho(t)e^{i\omega_L(t-t_0)I_z},\\
I_{x:\text{rot}}(t)&\equiv e^{(i/\hbar)(t-t_0)\mathcal{H}_{[A]}{}^{(0)}}I_x e^{-(i/\hbar)(t-t_0)\mathcal{H}_{[A]}{}^{(0)}}\\
&=I_x\cos[\omega_L(t-t_0)]+I_y\sin[\omega_L(t-t_0)],
\end{aligned}\tag{55}$$

so that

$$\langle\mu'\rangle_t=(\hbar\gamma/V_{[A]})\{\cos[\omega_L(t-t_0)]\,\text{Trace}(\rho_{\text{rot}}(t)I_x)+\sin[\omega_L(t-t_0)]\,\text{Trace}(\rho_{\text{rot}}(t)I_y)\}\tag{56}$$

identical with Eq. (I-154). In I it is also assumed on the basis of a physical argument that $\text{Trace}(\rho_{\text{rot}}(t)I_y)=0$; with this argument Eq. (56) becomes

$$\langle\mu'\rangle_t=(\hbar\gamma/V_{[A]})\cos[\omega_L(t-t_0)]\,\text{Trace}(\rho_{\text{rot}}(t)I_x).\tag{57}$$

We proceed to calculate $\rho_{\text{rot}}(t)$. Equations (55) and (53) yield

$$\rho_{\text{rot}}(t)=\rho(t_0)+(i/\hbar)\int_{t_0}^{t}[\rho_{\text{rot}}(t'),\mathcal{H}_{[B]:\text{rot}}{}^{(0)}(t')+V_{\text{rot}}(t')+\mathcal{H}_{\text{rf:rot}}(t')]dt',\tag{58}$$

with

$$\begin{aligned}
\mathcal{H}_{[B]:\text{rot}}{}^{(0)}(t')&\equiv e^{-i\omega_L(t'-t_0)I_z}\mathcal{H}_{[B]}{}^{(0)}e^{i\omega_L(t'-t_0)I_z}=\mathcal{H}_{[B]}{}^{(0)},\\
\mathcal{H}_{\text{rf:rot}}(t')&\equiv e^{-i\omega_L(t'-t_0)I_z}\mathcal{H}_{\text{rf}}(t')e^{i\omega_L(t'-t_0)I_z}=-\hbar\omega_1 I_x,\\
V_{\text{rot}}(t')&\equiv e^{-i\omega_L(t'-t_0)I_z}(V^{\text{secular}}+V^{\text{nonsecular}})e^{i\omega_L(t'-t_0)I_z}\\
&=V^{\text{secular}}+V_{\text{rot}}{}^{\text{nonsecular}}(t'),
\end{aligned}\tag{59}$$

---

[15] See for example, A. Redfield, Phys. Rev. **98**, 1787 (1955); W. I. Goldburg, *ibid.* **122**, 831 (1961); C. P. Slichter and W. C. Holton, *ibid.* **122**, 1701 (1961); M. Goldman, and A. Landesman, Compt. Rend. **252**, 263 (1961).

which is equivalent to

$$\sigma(t)\equiv e^{(i/\hbar)(t-t_0)\kappa}\rho_{\rm rot}(t)e^{-(i/\hbar)(t-t_0)\kappa}=\rho(t_0)+\frac{i}{\hbar}\int_{t_0}^{t}[\sigma(t'),U(t')]dt'$$

$$=\rho(t_0)+\frac{i}{\hbar}\int_{t_0}^{t}[\rho(t_0),U(t')]dt'+\text{terms}\sim\left(\frac{V^{\rm nonsecular}}{\mathcal{H}^{(0)}}\right)^2,\cdots, \tag{60}$$

with

$$\kappa\equiv-\hbar\omega_1I_x+\mathcal{H}_{[B]}{}^{(0)}+V^{\rm secular}\equiv\kappa^{(0)}+V^{\rm secular};$$
$$U(t)\equiv e^{(i/\hbar)(t-t_0)\kappa}V_{\rm rot}{}^{\rm nonsecular}(t)e^{-(i/\hbar)(t-t_0)\kappa}. \tag{61}$$

We are now ready to evaluate $\langle\mu'\rangle_t$ by substitution of Eqs. (60) and (61) into Eq. (57). We obtain, using also Eq. (I-10) and the fact that $[\kappa^{(0)},I_x]=0$,

$$\langle\mu'\rangle_t=(\hbar\gamma/V_{[A]})\cos[\omega_L(t-t_0)]\left\{\text{Trace}(e^{-(i/\hbar)(t-t_0)\kappa}\rho(t_0)e^{(i/\hbar)(t-t_0)\kappa}I_x)\right.$$
$$\left.+\left(\frac{i}{\hbar}\right)\int_{t_0}^{t}\text{Trace}([\rho(t_0),U(t')]I_x)dt'+\text{terms}\sim\left(\frac{V^{\rm secular}V^{\rm nonsecular}}{(\mathcal{H}^{(0)})^2}\right),\left(\frac{V^{\rm nonsecular}}{\mathcal{H}^{(0)}}\right)^2,\cdots\right\} \tag{62}$$

and note that the second term on the right side of Eq. (62) vanishes since

$$\text{Trace}([\rho(t_0),U(t')]I_x)=\text{Trace}([I_x,\rho(t_0)]U(t')) \tag{63}$$

for any three operators $\rho(t_0)$, $U(t')$, I_x, and since, on the basis of Eq. (55),

$$[I_x,\rho(t_0)]=0. \tag{64}$$

We therefore see from Eqs. (62)–(64), (57) that, apart from the there indicated higher order terms, the effective Hamiltonian for the time evolution in the rotating frame of the statistical configuration of $[A+B]$ is the κ of Eq. (61) where, for subsequent discussion, we identify $V^{\rm secular}$ with $V_{\rm dip\text{-}dip}{}^{\rm secular}$. Further, if $(V_{\rm dip\text{-}dip}{}^{\rm secular}/\kappa^{(0)})^3$, $(V_{\rm dip\text{-}dip}{}^{\rm secular}/\kappa^{(0)})^4$, $\cdots$ and $\{T_{\rm trans}{}^{-1}/[\omega_1+(kT_{\rm Debye}/\hbar)(T_{\rm latt}/T_{\rm Debye})^4]\}$ are all small compared to unity ($T_{\rm trans}$ is a characteristic relaxation time for the transverse magnetization and $T_{\rm latt}$ is the lattice temperature) a master equation holds for $P_{[A+B]\rm rot}(u;t)\equiv\langle u|\rho_{\rm rot}(t)|u\rangle\cong\langle u|e^{-(i/\hbar)(t-t_0)\kappa}\rho(t_0)e^{(i/\hbar)(t-t_0)\kappa}|u\rangle$ [see Sec. G of I and Eqs. (I-22)–(I-36)]. As a result we can introduce a time-dependent spin temperature in the rotating frame provided that $W_{[q]}{}^{\text{quasi-equil }[A]}(\mu_q-1/\mu_q;t)\gg w_{[q]}{}^{\rm equil}(\mu_q-1/\mu_q)$ where $\mu_q\doteq I_{[q]x}$ and where $W_{[q]}{}^{\text{quasi-equil }[A]}(\mu_q-1/\mu_q;t)$ and $w_{[q]}{}^{\rm equil}(\mu_q-1/\mu_q)$ arise, respectively, from $V_{\rm dip\text{-}dip}{}^{\text{secular flip-flop}}$ and $\{V_{\rm dip\text{-}dip}$ of nuclear spin-impurity electronic spin$\}$, the last interaction being appropriately expressed in the rotating frame.[16]

In concluding this section it is interesting to make a few further remarks about the $\langle\mu'\rangle_t$ of Eqs. (62)–(64):

$$\langle\mu'\rangle_t\cong(\hbar\gamma/V_{[A]})\cos[\omega_L(t-t_0)]\,\text{Trace}[e^{-(i/\hbar)(t-t_0)\kappa}\rho(t_0)e^{(i/\hbar)(t-t_0)\kappa}I_x],$$
$$\kappa=-\hbar\omega_1I_x+\mathcal{H}_{[B]}{}^{(0)}+V_{\rm dip\text{-}dip}{}^{\rm secular}\equiv\kappa^{(0)}+V_{\rm dip\text{-}dip}{}^{\rm secular}. \tag{65}$$

In the limit of a rigid lattice we have $[\mathcal{H}_{[B]}{}^{(0)},V_{\rm dip\text{-}dip}{}^{\rm secular}]=0$ (see Sec. G of I) and Eq. (65) becomes

$$\langle\mu'\rangle_t\cong(\hbar\gamma/V_{[A]})\cos[\omega_L(t-t_0)]\,\text{Trace}\{\exp[i\omega_1(t-t_0)I_x-(i/\hbar)(t-t_0)V_{\rm dip\text{-}dip}{}^{\rm secular}]\rho(t_0)$$
$$\times\exp[-i\omega_1(t-t_0)I_x+(i/\hbar)(t-t_0)V_{\rm dip\text{-}dip}{}^{\rm secular}]I_x\}, \tag{66}$$

which in the limit of $H_1\to0$ for $t>t_0$ is

$$\langle\mu'\rangle_t\cong(\hbar\gamma/V_{[A]})\cos[\omega_L(t-t_0)]\,\text{Trace}\{\exp[-(i/\hbar)(t-t_0)V_{\rm dip\text{-}dip}{}^{\rm secular}]\rho(t_0)\exp[(i/\hbar)(t-t_0)V_{\rm dip\text{-}dip}{}^{\rm secular}]I_x\} \tag{67}$$

identical with Eq. (I-175). Equation (67) predicts an oscillatory approach of $\{\langle\mu'\rangle_t/\cos[\omega_L(t-t_0)]\}$ to equilibrium—Lowe-Norberg beats—which is presumably absent when H_1 is introduced to the extent: $\hbar\gamma H_1\gtrsim\hbar^2\gamma^2/(r_{fg})_{\rm min}{}^3$ so that Eq. (66) applies. In this connection an explicit evaluation of the trace in Eq. (66) and performance of the corresponding $\langle\mu'\rangle_t$ vs t measurement would be of great interest since we believe that no Lowe-Norberg beats will be present *even* for a rigid lattice *if* $\hbar\gamma H_1\gtrsim\hbar^2\gamma^2/(r_{fg})_{\rm min}{}^3$. In fact, this last condition is necessary when the lattice is rigid for the validity of a master equation for $P_{[A+B]\rm rot}(u;t)$ (and hence for the absence of the beats) and is in that case essentially equivalent to the condition $(V_{\rm dip\text{-}dip}{}^{\rm secular}/\kappa^{(0)})^3$, $(V_{\rm dip\text{-}dip}{}^{\rm secular}/\kappa^{(0)})^4$, $\cdots\ll1$.

---

[16] Nuclear relaxation in the rotating frame due to spin diffusion to impurity electron spins is worked out in detail by I. Solomon and J. Ezratty, Phys. Rev. **127**, 78 (1962).

V. THE LAW OF ENTROPY VARIATION AND TIME-DEPENDENT TEMPERATURES

We develop in this section equations for the evolution in time of the "individual particle entropy":

$$S_{[q]}(t) \equiv -k \sum_{u^{(q)}} P_{[q]}(u^{(q)};t) \ln P_{[q]}(u^{(q)};t). \tag{68}$$

Comparison of Eq. (I-67) with Eq. (68) indicates that the entropy of the system of interest $[A]$:

$$S_{[A]}(t) \equiv -k \sum_{\{u^{(i)}\}} P_{[A]}(\{u^{(i)}\};t) \ln P_{[A]}(\{u^{(i)}\};t) = N_{[A]} S_{[q]}(t), \tag{69}$$

if

$$P_{[A]}(\{u^{(i)}\};t) = \prod_p P_{[p]}(u^{(p)};t) = [P_{[q]}(u^{(q)};t)]^{N_{[A]}}, \tag{70}$$

the last relation being consistent with the definition of $P_{[q]}(u^{(q)};t)$ in Eq. (18) or Eqs. (5) and (6), for individual particles which are identical and effectively independent. Equation (69) shows that in statistical configurations of $[A]$ in which $S_{[A]}(t)$ is extensive, $S_{[q]}(t)$ is independent of $N_{[A]}$.

Equations (68), (17), and (18) yield

$$\begin{aligned}\frac{dS_{[q]}(t)}{dt} = \frac{k}{2} \sum_{u^{(q)},v^{(q)}} \{&[W_{[q]}(u^{(q)}/v^{(q)};t) + w_{[q]}(u^{(q)}/v^{(q)};t)] P_{[q]}(v^{(q)};t) \\ &- [W_{[q]}(v^{(q)}/u^{(q)};t) + w_{[q]}(v^{(q)}/u^{(q)};t)] P_{[q]}(u^{(q)};t)\} \ln\left[\frac{P_{[q]}(v^{(q)};t)}{P_{[q]}(u^{(q)};t)}\right],\end{aligned} \tag{71}$$

which is to be compared with Eq. (I-68). Defining further the net heat flow from $[B]$ to $[A]$ per particle as

$$\frac{dQ_{[q]}(t)}{dt} \equiv \sum_{u^{(q)}} \epsilon(u^{(q)}) \frac{dP_{[q]}(u^{(q)};t)}{dt}, \tag{72}$$

[see the analogous Eq. (I-70)] and using Eqs. (27) and (28) we obtain

$$\frac{dQ_{[q]}(t)}{dt} = \tfrac{1}{2} \sum_{u^{(q)},v^{(q)}} [\epsilon(u^{(q)}) - \epsilon(v^{(q)})][w_{[q]}(u^{(q)}/v^{(q)};t) P_{[q]}(v^{(q)};t) - w_{[q]}(v^{(q)}/u^{(q)};t) P_{[q]}(u^{(q)};t)]. \tag{73}$$

It is to be noted that our $dQ_{[q]}(t)/dt$ is to be identified with the $d\langle\epsilon_{[q]}\rangle_t/dt$ of Eqs. (27) and (28) and differs from the time rate of change of the internal energy per particle:

$$\begin{aligned}\frac{dU_{[q]}(t)}{dt} &= \frac{d}{dt} \sum_{u^{(q)}} \epsilon(u^{(q)}) P_{[q]}(u^{(q)};t) \\ &= \sum_{u^{(q)}} \epsilon(u^{(q)}) (dP_{[q]}(u^{(q)};t)/dt) - \sum_{u^{(q)}} \left(-\frac{\partial \epsilon(u^{(q)})}{\partial V_{[A]}}\right) \frac{dV_{[A]}}{dt} = \frac{dQ_{[q]}(t)}{dt} - p_{[A]} \frac{dV_{[A]}}{dt},\end{aligned} \tag{74}$$

by a term which represents the work per particle per unit time by $[A]$ on $[B]$ [see the analogous Eqs. (I-69), (I-70)]. Introducing the quantities $\delta_{[q]}(u^{(q)};t)$, $\lambda_{[q]}(u^{(q)}/v^{(q)})$, $\Delta_{[q]}(u^{(q)};t)$, $\Lambda_{[q]}(u^{(q)}/v^{(q)};t)$ and referring to Eqs. (26), (34), and (30) we have

$$\begin{aligned}\delta_{[q]}(u^{(q)};t) &\equiv \frac{P_{[q]}(u^{(q)};t) - P_{[q]}{}^{\text{equil}}(u^{(q)})}{P_{[q]}{}^{\text{equil}}(u^{(q)})}, \\ \lambda_{[q]}(u^{(q)}/v^{(q)}) &\equiv w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)}) P_{[q]}{}^{\text{equil}}(v^{(q)}) = w_{[q]}{}^{\text{equil}}(v^{(q)}/u^{(q)}) P_{[q]}{}^{\text{equil}}(u^{(q)}) \equiv \lambda_{[q]}(v^{(q)}/u^{(q)}), \\ \Delta_{[q]}(u^{(q)};t) &\equiv \frac{P_{[q]}(u^{(q)};t) - P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)}{P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)} \equiv \frac{D_{[q]}(u^{(q)};t)}{P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)}, \\ \Lambda_{[q]}(u^{(q)}/v^{(q)};t) &\equiv W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t) P_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)};t) \\ &= W_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)}/u^{(q)};t) P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t) \equiv \Lambda_{[q]}(v^{(q)}/u^{(q)};t),\end{aligned} \tag{75}$$

so that, replacing $W_{[q]}(u^{(q)}/v^{(q)};t)$, $w_{[q]}(u^{(q)}/v^{(q)};t)$ in Eqs. (71) and (73) by $W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)$, $w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})$ [see Eq. (32) and associated discussion] and combining Eqs. (75), (73), and (71) we finally obtain

$$\frac{dS_{[q]}(t)}{dt}=\frac{k}{2}\sum_{u^{(q)},v^{(q)}}\Lambda_{[q]}(u^{(q)}/v^{(q)};t)[\Delta_{[q]}(u^{(q)};t)-\Delta_{[q]}(v^{(q)};t)]\ln\left[\frac{1+\Delta_{[q]}(u^{(q)};t)}{1+\Delta_{[q]}(v^{(q)};t)}\right]$$
$$+\frac{k}{2}\sum_{u^{(q)},v^{(q)}}\lambda_{[q]}(u^{(q)}/v^{(q)})[\delta_{[q]}(u^{(q)};t)-\delta_{[q]}(v^{(q)};t)]\ln\left[\frac{1+\delta_{[q]}(u^{(q)};t)}{1+\delta_{[q]}(v^{(q)};t)}\right]+\frac{1}{T}\frac{dQ_{[q]}(t)}{dt}, \tag{76}$$

$$\frac{dQ_{[q]}(t)}{dt}=-\tfrac{1}{2}\sum_{u^{(q)},v^{(q)}}\lambda_{[q]}(u^{(q)}/v^{(q)})[\delta_{[q]}(u^{(q)};t)-\delta_{[q]}(v^{(q)};t)][\epsilon(u^{(q)})-\epsilon(v^{(q)})], \tag{77}$$

which is to be compared with Eqs. (I-74) and (I-72). Equation (76) describes the evolution in time of the individual particle entropy and may be analyzed as follows: The first and second terms on the right side of Eq. (76) are each always $\geqq 0$ and represent time rates of change of the individual particle entropy associated with the tendency of the system of interest [A] to attain quasi-equilibrium and equilibrium, respectively—these two terms are second order in the deviations from quasi-equilibrium and equilibrium, $\Delta_{[q]}(u^{(q)};t)$ and $\delta_{[q]}(u^{(q)};t)$. The third term on the right side of Eq. (76) represents the time rate of change in the individual particle entropy associated with the net heat flow from [B] to [A] and may be >0 or <0—this third term is first order in the $\delta_{[q]}(u^{(q)};t)$ [Eq. (77)] and hence dominates the first two terms for sufficiently small deviations from quasi-equilibrium and equilibrium and for sufficiently low temperature.

We proceed to discuss several cases of physical interest on the basis of Eq. (76). Consider in particular the situation where $W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)\gg w_{[q]}{}^{\text{equil}}(u^{(q)}/v^{(q)})$ so that the system of interest [A] is properly characterized for $t-t_0\gtrsim T_{\text{quasi-equil }[A]}$ by a time-dependent temperature $\Theta_{[A]}(t)$ [Eqs. (33)–(45)]. Under these circumstances. and confining ourselves to times such that $t-t_0\gtrsim T_{\text{quasi-equil }[A]}$, Eq. (76) becomes

$$\frac{dS_{[q]}(t)}{dt}\cong\frac{k}{2}\sum_{u^{(q)},v^{(q)}}\Lambda_{[q]}(u^{(q)}/v^{(q)};t)[\Delta_{[q]}(u^{(q)};t)-\Delta_{[q]}(v^{(q)};t)]^2$$
$$-\frac{k}{2}\sum_{u^{(q)},v^{(q)}}\lambda_{[q]}(u^{(q)}/v^{(q)})[\delta_{[q]}(u^{(q)};t)-\delta_{[q]}(v^{(q)};t)][\epsilon(u^{(q)})-\epsilon(v^{(q)})]\left[\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right]+\frac{1}{T}\frac{dQ_{[q]}(t)}{dt}$$
$$=\frac{k}{2}\sum_{u^{(q)},v^{(q)}}\Lambda(u^{(q)}/v^{(q)};t)[\Delta_{[q]}(u^{(q)};t)-\Delta_{[q]}(v^{(q)};t)]^2+\frac{1}{T_{[A]}(t)}\frac{dQ_{[q]}(t)}{dt}, \tag{78}$$

where we have also used Eqs. (77), (34), and (26).

We can now distinguish two cases depending on whether

$$\frac{k}{2}\sum_{u^{(q)},v^{(q)}}\Lambda(u^{(q)}/v^{(q)};t)[\Delta_{[q]}(u^{(q)};t)-\Delta_{[q]}(v^{(q)};t)]^2\ll\text{or}\approx\frac{1}{T_{[A]}(t)}\frac{dQ_{[q]}(t)}{dt}, \tag{79}$$

which, using Eqs. (75), (77), and the estimate for $D_{[q]}(u^{(q)};t)$ given after Eqs. (36) and (37), is roughly equivalent to

$$\frac{w^{\text{equil}}(u^{(q)}/v^{(q)})}{W^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)}\ll\text{or}\approx\left(\frac{P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)}{P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)-P_{[q]}{}^{\text{equil}}(u^{(q)})}\right)\left(\frac{\epsilon(u^{(q)})}{\Theta_{[A]}(t)}\right). \tag{80}$$

Thus, in the case of the $\ll$ sign, Eq. (78) becomes the intuitively expected and often used

$$\frac{dS_{[q]}(t)}{dt}=\frac{1}{T_{[A]}(t)}\frac{dQ_{[q]}(t)}{dt}, \tag{81}$$

while, in the case of the $\approx$ sign, the terms $\sim(\Delta_{[q]}(u^{(q)};t)-\Delta_{[q]}(v^{(q)};t))^2$ on the right side of Eq. (78) contribute appreciably to $dS_{[q]}(t)/dt$. In view of Eq. (80) and the assumed $W^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)\gg w^{\text{equil}}(u^{(q)}/v^{(q)})$ this last case can hold only if $[P_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)};t)-P_{[q]}{}^{\text{equil}}(u^{(q)})]/P_{[q]}{}^{\text{equil}}(u^{(q)})$ is not too small (i.e., if $T_{\text{equil}}\gg t-t_0\gtrsim T_{\text{quasi-equil }[A]}$) and if $\epsilon(u^{(q)})\ll\Theta_{[A]}(t)$.

ACKNOWLEDGMENTS

One of the authors (A. Sher) wishes to thank Professor A. Abragam and Dr. M. W. Muller for very helpful discussions.

APPENDIX A

There is a third case where Eqs. (36) and (37) simplify sufficiently so that an explicit solution can be found for $\Theta_{[A]}(t)$. This is the case characterized by $\epsilon(u^{(q)})-\epsilon(0^{(q)})\ll\Theta_{[A]}(t)$, $\Theta_{[A]}$ for all important states $u^{(q)}$. In this approximation Eqs. (36) and (37) reduce to the expression

$$\frac{d\beta(t)}{dt}\cong -w_{[q]}(0^{(q)}/1^{(q)})[1-e^{-\beta(t)}]/e^{-\beta(t)}, \tag{A1}$$

where

$$\beta(t)\equiv[\epsilon(1^{(q)})-\epsilon(0^{(q)})]\left[\frac{1}{\Theta_{[A]}(t)}-\frac{1}{\Theta_{[A]}}\right]. \tag{A2}$$

The solution of Eq. (A1) is

$$e^{-\beta(t)}=1-[1-e^{-\beta(t^*)}]\exp[-w_{[q]}(0^{(q)}/1^{(q)})(t-t^*)];\quad t-t_0\gtrsim t^*-t_0\equiv T_{\text{quasi-equil }[A]}. \tag{A3}$$

We note that for times t for which the system has almost returned to equilibrium, i.e., for $\Theta_{[A]}(t)\cong\Theta_{[A]}$ and so $\beta\ll 1$, Eq. (A3) reduces to Eq. (43).

The average value of the energy of the qth individual particle, $\langle\epsilon_{[q]}\rangle_t$, is here given by

$$\langle\epsilon_{[q]}\rangle_t=\sum_{u^{(q)}}\epsilon(u^{(q)})[e^{-\epsilon(u^{(q)})/\theta_{[A]}(t)}/\sum_{v^{(q)}}e^{-\epsilon(v^{(q)})/\theta_{[A]}(t)}]$$

$$\cong\epsilon(0^{(q)})+[\epsilon(1^{(q)})-\epsilon(0^{(q)})]\exp\{[\epsilon(1^{(q)})-\epsilon(0^{(q)})]/\Theta_{[A]}\}e^{-\beta(t)},$$

whence, substituting from Eq. (A3),

$$\epsilon_{[q]}\rangle_t-\epsilon(0^{(q)})=[\epsilon(1^{(q)})-\epsilon(0^{(q)})]\exp\{-[\epsilon(1^{(q)})-\epsilon(0^{(q)})]/\Theta_{[A]}\}\times\{1-[1-e^{-\beta(t^*)}]\exp[-w(0^{(q)}/1^{(q)})(t-t^*)]\}. \tag{A4}$$

APPENDIX B

We wish to calculate $W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}/v^{(q)};t)$ arising from a secular dipole-dipole interaction. We take $\mathcal{H}_{[A]}{}^{(0)}=-\hbar\gamma H_0 I_z=-\sum_g\hbar\gamma H_0 I_{[g]z}$ and $u^{(q)}=m_q\doteq I_{[q]z}$, $v^{(q)}=m_q\pm1$. We also suppose that the temperature is so low that $\mathbf{r}_{fg}\equiv\mathbf{R}_{fg}+\boldsymbol{\xi}_{fg}\cong\mathbf{R}_{fg}$, i.e., assume the rigid lattice approximation [see Eq. (I-168) *et seq.*]. Equation (I-168) then becomes

$$V_{\text{dip-dip}}{}^{\text{secular}}=\tfrac{1}{2}\sum_{f,g}A_{fg}\{\tfrac{1}{2}[I_{[f]+}I_{[g]-}+I_{[f]-}I_{[g]+}]-2I_{[f]z}I_{[g]z}\}$$

$$\equiv V_{\text{dip-dip}}{}^{\text{secular flip-flop}}+\tfrac{1}{2}\sum_{f,g}A_{fg}\{-2I_{[f]z}I_{[g]z}\}, \tag{B1}$$

and

$$A_{fg}\cong-\tfrac{1}{2}(\hbar^2\gamma^2/R_{fg}{}^3)(1-3\cos^2\Theta_{fg}),$$

$$\langle\eta_u,\beta_u|\sum_{f,g}A_{fg}|\eta_v,\beta_v\rangle=\delta(\eta_u,\eta_v)\langle\beta_u|\sum_{f,g}A_{fg}|\beta_u'\rangle=\delta(\eta_u,\eta_v)\delta(\beta_u,\beta_u')\sum_{f,g}A_{fg}, \tag{B2}$$

while Eq. (18) yields

$$W_{[q]}{}^{\text{quasi-equil }[A]}(u^{(q)}=m_q/v^{(q)}=m_q-1;t)$$

$$=\left[\sum_{\{u^{(i)}\}^{(q)},\{v^{(i)}\}^{(q)};\beta_u,\beta_v}\frac{W_{[A+B]}(\{u^{(i)}\};E-\epsilon_u,\beta_u/\{v^{(i)}\};E-\epsilon_v,\beta_v)}{\mathfrak{N}_{[B]}(E-\epsilon_v)}\times P_{[A]}{}^{\text{quasi-equil }[A]}(\{v^{(i)}\};t)\delta(\epsilon_u,\epsilon_v)\right]\Big/P_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)};t)$$

$$=\left[\sum_{\{u^{(i)}\}^{(q)},\{v^{(i)}\}^{(q)};\beta_u,\beta_u'}\frac{W_{[A+B]}(\{u^{(i)}\};E-\epsilon_u,\beta_u/\{v^{(i)}\};E-\epsilon_u,\beta_u')}{\mathfrak{N}_{[B]}(E-\epsilon_u)}\times P_{[A]}{}^{\text{quasi-equil }[A]}(\{v^{(i)}\};t)\delta(\epsilon_u,\epsilon_v)\right]\Big/P_{[q]}{}^{\text{quasi-equil }[A]}(v^{(q)};t). \tag{B3}$$

The nonvanishing

$$W_{[A+B]}(\{u^{(i)}\};E-\epsilon_u,\beta_u/\{v^{(i)}\};E-\epsilon_u;\beta_u')=\delta(\beta_u,\beta_u')W_{[A+B]}(\{u^{(i)}\};E-\epsilon_u,\beta_u/\{v^{(i)}\};E-\epsilon_u,\beta_u)$$

contributing to Eq. (B3) arise from $V_{\text{dip-dip}}{}^{\text{secular flip-flop}}$ which is here identical with V_A and we have, using Eqs. (8) and (B1),

$$\begin{aligned}
&W_{[A+B]}(\{m_i\}^{(q)(p)},m_q,m_p;E-\epsilon_u,\beta_u/\{m_i'\}^{(q)(p)},m_q-1,m_p+1;E-\epsilon_u,\beta_u)\\
&=\frac{2\pi}{\hbar}\delta(\epsilon_u-\epsilon_v)|\langle\{m_i\}^{(q)(p)},m_q,m_p;E-\epsilon_u,\beta_u|\tfrac{1}{4}\sum_{f,g}A_{fg}(I_{[f]+}I_{[g]-}+I_{[f]-}I_{[g]+})\\
&\qquad\qquad\times|\{m_i'\}^{(q)(p)},m_q-1,m_p+1;E-\epsilon_u,\beta_u\rangle|^2\\
&=\frac{\pi}{8\hbar}\delta(\epsilon_u-\epsilon_v)(I-m_q+1)(I+m_q)\sum_p A_{qp}{}^2(I-m_p)(I+m_p+1)\delta(\{m_i'\}^{(q)(p)},\{m_i\}^{(q)(p)})\delta(m_p',m_p+1),
\end{aligned}\tag{B4}$$

where $\delta(\epsilon_u-\epsilon_v)=\delta(\sum_i m_i-\sum_i m_i')/\hbar\gamma H_0$ is a Dirac delta function. Equations (B4) and (B3) yield

$$\begin{aligned}
&W_{[q]}{}^{\text{quasi-equil }[A]}(m_q/m_q-1;t)\\
&=\frac{(\pi/8\hbar)(I-m_q+1)(I+m_q)}{\exp[-\epsilon(m_q-1)/\Theta_{[A]}(t)]}\sum_p A_{qp}{}^2\sum_{\{m_i\}^{(q)},\{m_i'\}^{(q)}}\{[\delta(\textstyle\sum_i m_i-\sum_i m_i')/\hbar\gamma H_0]\\
&\qquad\times\delta(\{m_i'\}^{(q)(p)},\{m_i\}^{(q)(p)})\delta(m_p',m_p+1)P_{[A]}{}^{\text{quasi-equil }[A]}(\{m_i'\};t)(I-m_p)(I+m_p+1)\},
\end{aligned}\tag{B5}$$

and inserting the approximation

$$P_{[A]}{}^{\text{quasi-equil }[A]}(\{m_i'\};t)\cong\prod_i P_{[i]}{}^{\text{quasi-equil }[A]}(m_i';t)=\prod_i e^{-\epsilon(m_i')/\Theta_{[A]}(t)}/\{\sum_{m_i}e^{-\epsilon(m_i)/\Theta_{[A]}(t)}\}$$

into Eq. (B5), we obtain

$$W_{[q]}{}^{\text{quasi-equil }[A]}(m_q/m_q-1;t)=(I-m_q+1)(I+m_q)\frac{e^{\hbar\gamma H_0/\Theta_{[A]}(t)}}{\{\sum_{m_q}e^{m_q\hbar\gamma H_0/\Theta_{[A]}(t)}\}}W_{[q]}(t),\tag{B6}$$

where

$$\begin{aligned}
&W_{[q]}(t)\equiv\frac{\pi}{8}(\gamma H_0)\sum_p\left(\frac{A_{qp}}{\hbar\gamma H_0}\right)^2[I(I+1)-\langle m_p{}^2\rangle_t{}^{\text{quasi-equil }[A]}-\langle m_p\rangle_t{}^{\text{quasi-equil }[A]}],\\
&\langle m_p{}^n\rangle_t{}^{\text{quasi-equil }[A]}\equiv\sum_{m_p}m_p{}^n\frac{e^{-\epsilon(m_p)/\Theta_{[A]}(t)}}{\{\sum_{m_p'}e^{-\epsilon(m_p')/\Theta_{[A]}(t)}\}};\quad n=1,2,\cdots.
\end{aligned}\tag{B7}$$