15 *Irreversible processes and fluctuations*

IN THIS final chapter we shall attempt to make some general statements about systems which are not necessarily in equilibrium. Thus we shall examine how equilibrium is approached and how rapidly it is approached. We shall also want to gain an understanding of the frictional effects (like those due to viscous forces or to electrical resistance) which lead to dissipation of energy in many systems of interest. Finally, we shall investigate the fluctuations exhibited by certain parameters of systems in thermal *equilibrium*. Although these various questions may at first sight seem unrelated, our discussion will show that they are actually very intimately connected.

TRANSITION PROBABILITIES AND MASTER EQUATION

15·1 *Isolated system*

Consider an isolated system A. Let its Hamiltonian (or energy) be

$$\mathcal{H}_0 = \mathcal{H} + \mathcal{H}_i \tag{15·1·1}$$

where $\mathcal{H}$ is the main part of the Hamiltonian and $\mathcal{H}_i \ll \mathcal{H}$ is a small additional part describing some weak interactions not included in $\mathcal{H}$. (For example, in the case of a dilute gas, $\mathcal{H}$ might contain all the kinetic energy terms of the molecules, while $\mathcal{H}_i$ might describe the small interactions between the molecules.) Let the quantum states of $\mathcal{H}$ be denoted by r and their corresponding energy levels by E_r. If $\mathcal{H}_i = 0$, these states would be quantum states of the total Hamiltonian so that the system A would remain in any such state indefinitely. The presence of the additional interaction $\mathcal{H}_i$ makes this no longer true, since $\mathcal{H}_i$ is capable of inducing transitions between the various unperturbed states r. If $\mathcal{H}_i$ is small, if there is a nearly continuous distribution of

accessible energy levels,* and if one considers time intervals which are not too small, then there exists a well-defined transition probability W_{rs} per unit time from the unperturbed state r to the unperturbed state s of system A. By conservation of energy W_{rs} is such that

$$W_{rs} = 0 \quad \text{if } E_r \neq E_s, \tag{15·1·2}$$

Furthermore, there is a symmetry property relating this transition to the inverse transition* from state s to state r,

$$W_{sr} = W_{rs} \tag{15·1·3}$$

***Remark** This follows from the fact that by quantum mechanics

$$W_{rs} \propto |\langle s|\mathcal{H}_i|r\rangle|^2 = \langle s|\mathcal{H}_i|r\rangle^*\langle s|\mathcal{H}_i|r\rangle$$

where $\langle s|\mathcal{H}_i|r\rangle$ is the matrix element of $\mathcal{H}_i$ between state r and state s. Since $\mathcal{H}_i$ is hermitian, so that $\langle s|\mathcal{H}_i|r\rangle = \langle r|\mathcal{H}_i|s\rangle^*$, the relation (15·1·3) follows immediately. Note also that this symmetry property relating *inverse* transitions is not quite the same as the symmetry property between *reverse* transitions discussed in (9·15·2).

Let $P_r(t)$ denote the probability that system A is found in state r at time t. Then P_r tends to increase with time because systems in other states make transitions to the given state r, and it tends to decrease because systems in this state r make transitions to other states s. The time dependence of P_r can thus be described by the equation

$$\frac{dP_r}{dt} = \sum_s P_s W_{sr} - \sum_s P_r W_{rs} \tag{15·1·4}$$

or

$$\frac{dP_r}{dt} = \sum_s (P_s W_{sr} - P_r W_{rs}) \tag{15·1·5}$$

If there are N states, one can write N such equations in the corresponding number of unknowns P_r. Hence a knowledge of the transition probabilities W_{rs} allows one to compute the probabilities P_r as a function of time.

Equation (15·1·5) is called the "master equation." Note that all terms in it are real and that the time t enters linearly in the first derivative. Hence the master equation does *not* remain invariant as the sign of the time t is reversed from t to $-t$. This equation describes, therefore, the *irreversible* behavior of a system. It is thus quite unlike the detailed microscopic equations of motion, e.g., the Schrödinger equation, which provide a description which

* This can be the case because the energy levels are very closely spaced, or because one considers an ensemble of systems not all of which have exactly the same energy levels. (An example of the latter situation might be an assembly of nuclei located in slightly different local magnetic fields.)

is invariant under time-reversal.* Although the master equation is related to the Schrödinger equation, the precise approximations which lead to the derivation of the master equation are subtle and involve the interesting question of how one passes from reversible microscopic equations to a description which exhibits irreversibility.† We shall discuss this question in somewhat greater detail in Sec. 15·7. In the present context the approximations involved are those, already mentioned, which lead to the existence of well-defined transition probabilities per unit time and those implied by a discussion which concerns itself only with the *probability* P_r that the system is in a given state r. (The complete quantum-mechanical specification of the state of the system at all times involves the complex *probability amplitude* $a_r(t)$, where $P_r = |a_r|^2$. The present discussion thus involves approximations which disregard all information contained in the phases of the amplitudes a_r.)

If the isolated system A is in equilibrium, the fundamental statistical postulate of equal a priori probabilities asserts that, for all r and s,

$$P_r = P_s \tag{15·1·6}$$

By the symmetry property (15·1·3) the right side of (15·1·5) gives then

$$P_s W_{sr} - P_r W_{rs} = P_s(W_{sr} - W_{rs}) = 0 \tag{15·1·7}$$

so that (15·1·5) yields $dP_r/dt = 0$ for all r. Thus Eq. (15·1·5) does then describe correctly an equilibrium situation.

The relation (15·1·7) expresses a condition of detailed balance according to which the rate of occurrence of *any* transition equals the corresponding rate of occurrence of the *inverse* transition; i.e., states of the same energy (for which $W_{rs} \neq 0$) are connected by the relation

$$P_r W_{rs} = P_s W_{sr} \tag{15·1·8}$$

This is certainly a sufficient condition to guarantee that $dP_r/dt = 0$ for all r; it is not, however, a necessary condition. As we have just shown, the condition (15·1·8) is satisfied in equilibrium. It may, however, be possible to encounter nonequilibrium steady-state situations, defined by the fact that $dP_r/dt = 0$ for all r, in which the condition (15·1·8) is *not* satisfied.‡

Note that if it is *assumed* that the condition of detailed balance holds in an equilibrium situation where $P_r = P_s$, then one can immediately conclude from (15·1·8) that $W_{sr} = W_{rs}$. Since the transition probabilities W are dynamical quantities which do not depend on whether the system is in equilibrium or not, it then follows that the relation $W_{sr} = W_{rs}$ must be quite generally valid even if A is not in equilibrium. Thus one arrives again at the result (15·1·3).

* For a discussion of time-reversal invariance, see R. C. Tolman, "The Principles of Statistical Mechanics," secs. 37 and 95, Oxford University Press, Oxford, 1938.

† For a discussion of such derivations and further references, see R. W. Zwanzig in University of Colorado "Lectures in Theoretical Physics," vol. 3, pp. 106–141, Interscience Publishers, New York, 1961.

‡ See, for example, M. J. Klein, *Phys. Rev.* vol. 97, p. 1446 (1955).

15·2 System in contact with a heat reservoir

Consider a system A in thermal contact with a much larger system A'. The total Hamiltonian of the combined system $A^{(0)} = A + A'$ is

$$\mathcal{H}^{(0)} = \mathcal{H} + \mathcal{H}' + \mathcal{H}_i$$

where $\mathcal{H}$ is the Hamiltonian of A, $\mathcal{H}'$ is that of the heat reservoir A', and $\mathcal{H}_i$ is very small and describes the weak interaction between A and A'. In the absence of interaction when $\mathcal{H}_i = 0$, denote the energy of A in state r by E_r, and the energy of A' in state r' by $E'_{r'}$. The presence of the interaction $\mathcal{H}_i$ induces transitions between these states and is responsible for bringing about equilibrium between A and A'.

Let P_r be the probability that A is in state r, and $P'_{r'}$ the corresponding probability that A' is in state r'. The state of the combined system $A^{(0)}$ is described by the pair of numbers r and r'; the probability of $A^{(0)}$ being in this state is $P^{(0)}_{rr'} = P_r P'_{r'}$. In this combined system the interaction $\mathcal{H}_i$ causes transitions between states. Under assumptions similar to those of the last subsection, there exists a well-defined transition probability $W^{(0)}(rr' \to ss')$ per unit time from state rr' to state ss'. By conservation of energy,

$$W^{(0)}(rr' \to ss') = 0 \quad \text{if } E_r + E'_{r'} \neq E_s + E'_{s'}, \tag{15·2·1}$$

In addition, (15·1·3) yields for the isolated system $A^{(0)}$ the symmetry condition

$$W^{(0)}(ss' \to rr') = W^{(0)}(rr' \to ss') \tag{15·2·2}$$

Let us first recall the relations valid in equilibrium. Then P_r is proportional to the total number of states available to $A^{(0)}$ when A is known to be in the given state r; thus, by the reasoning of Sec. 6·2,

$$P_r \propto 1 \cdot \Omega'(E^{(0)} - E_r) \propto e^{-\beta E_r} \tag{15·2·3}$$

where $\Omega'(E')$ is the number of states available to A' when its energy is E', $E^{(0)}$ is the constant total energy of $A^{(0)}$, and $\beta \equiv \partial \ln \Omega'/\partial E'$ (evaluated for $E' = E^{(0)}$) is the temperature parameter of the reservoir A'.

One can also obtain the canonical distribution (15·2·3) for system A by assuming that the condition of detailed balance prevails in equilibrium and that the interaction between A and A' causes transitions between all states of A. Then one can write

$$P_r P'_{r'} W^{(0)}(rr' \to ss') = P_s P'_{s'} W^{(0)}(ss' \to rr') \tag{15·2·4}$$

where $W^{(0)} \neq 0$. Using the equality (15·2·2) this becomes

$$\frac{P_r}{P_s} = \frac{P'_{s'}}{P'_{r'}} \tag{15·2·5}$$

But A' itself satisfies the canonical distribution, since the equilibrium of A' is undisturbed when it is placed in contact with a heat reservoir at temperature β. Hence $P'_{r'} \propto \exp(-\beta E'_{r'})$ and (15·2·5) becomes

$$\frac{P_r}{P_s} = \frac{e^{-\beta E'_{s'}}}{e^{-\beta E'_{r'}}} = e^{-\beta(E'_{s'} - E'_{r'})} \tag{15·2·6}$$

Application of the conservation of energy to (15·2·4) requires that

$$E_r + E'_{r'} = E_s + E'_{s'} \qquad \text{or} \qquad E'_{s'} - E'_{r'} = -(E_s - E_r)$$

Hence (15·2·6) becomes

$$\frac{P_r}{P_s} = e^{-\beta(E_r - E_s)} = \frac{e^{-\beta E_r}}{e^{-\beta E_s}} \tag{15·2·7}$$

and one regains the canonical distribution (15·2·3) for system A.

Suppose now that we consider a general *nonequilibrium* situation, but assume that the heat reservoir A' is so large that, irrespective of what A does, A' always remains in internal equilibrium. Thus, no matter what total energy A' may have at any one time, A' is always supposed to be distributed according to a canonical distribution with the constant temperature parameter β. Under these circumstances, let us ask for the net transition probability W_{rs} per unit time of the subsystem A from its state r to its state s. It should be clear that $W_{rs} \neq W_{sr}$; Fig. 15·2·1 illustrates how this comes about.

The transition probability W_{rs} can be obtained by multiplying the transition probability $W^{(0)}(rr' \to ss')$ for the combined system $A^{(0)}$ by the probability $P'_{r'}$ that A' is in the particular state r' and then summing over all possible initial states r' in which A' can be found and all the possible final states s' in which it can end up. Thus

$$W_{rs} = \sum_{r's'} P_{r'} W^{(0)}(rr' \to ss') = C \sum_{r's'} e^{-\beta E'_{r'}} W^{(0)}(rr' \to ss') \tag{15·2·8}$$

since $P'_{r'} = C \exp(-\beta E'_{r'})$, where C is some constant. Similarly,

$$W_{sr} = C \sum_{r's'} e^{-\beta E'_{s'}} W^{(0)}(ss' \to rr') \tag{15·2·9}$$

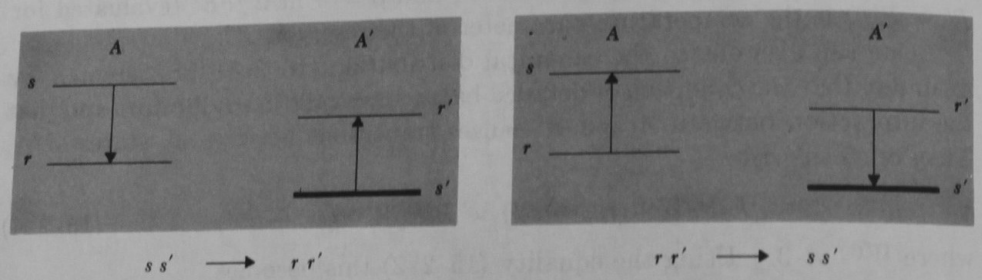

Fig. 15·2·1 ***Diagram illustrating a system A in thermal contact with a heat reservoir A'. The lines indicate the energy levels for states r and s of A, and states r' and s' of A'. Since A' remains always in thermal equilibrium, A' is more likely to be in the lower state s' (marked by the heavy line) than in the upper state r'. As a result, transitions of the type $ss' \to rr'$, illustrated in the left diagram, occur more frequently than those of type $rr' \to ss'$, illustrated on the right. Hence $W_{sr} > W_{rs}$. These transitions tend thus to produce the thermal equilibrium distribution where A is more likely to be in state r than in state s.***

But the energy conservation (15·2·1) implies that $E'_{s'} = E'_{r'} + E_r - E_s$. Using the symmetry relation (15·2·2), the expression (15·2·9) becomes then

$$W_{sr} = C \sum_{r's'} e^{-\beta E_{r'}} e^{-\beta(E_r - E_s)} W^{(0)}(rr' \to ss') = e^{-\beta(E_r - E_s)} W_{rs}$$

Thus

$$\frac{W_{sr}}{W_{rs}} = e^{-\beta(E_r - E_s)} = \frac{e^{-\beta E_r}}{e^{-\beta E_s}} \tag{15·2·10}$$

In the ordinary case where $\beta > 0$, $W_{sr} > W_{rs}$ if $E_s > E_r$. In the system A transitions to states of lower energy are thus more probable than transitions in the opposite direction. This is, of course, what is required to bring about the thermal equilibrium distribution in A. Indeed, if it is *assumed* that the condition of detailed balance prevails at equilibrium, then

$$P_r W_{rs} = P_s W_{sr} \tag{15·2·11}$$

The canonical distribution (15·2·7) then implies immediately the relation (15·2·10) between transition probabilities.

It is convenient to make the relationship (15·2·10) apparent by introducing a quantity $\lambda_{rs} = \lambda_{sr}$ defined by

$$e^{-\beta E_s} W_{sr} = e^{-\beta E_r} W_{rs} \equiv \lambda_{rs} \equiv \lambda_{sr}$$

Then one can write

$$W_{sr} = e^{\beta E_s} \lambda_{sr}, \qquad W_{rs} = e^{\beta E_r} \lambda_{rs} \tag{15·2·12}$$

and (15·2·10) follows automatically since $\lambda_{sr} = \lambda_{rs}$.

The probabilities for system A satisfy again the master equation (15·1·5)

$$\frac{dP_r}{dt} = \sum_s (P_s W_{sr} - P_r W_{rs}) = \sum_s \lambda_{sr}(P_s e^{\beta E_s} - P_r e^{\beta E_r}) \tag{15·2·13}$$

Once again, if equilibrium prevails so that the canonical distribution (15·2·3) holds for system A, then the right side of (15·2·13) vanishes and $dP_r/dt = 0$ for all r, as it should.

15·3 *Magnetic resonance*

An instructive and important example of the ideas developed in the preceding sections is that of magnetic resonance. Consider a substance containing N noninteracting nuclei (or electrons) of spin $\frac{1}{2}$ and magnetic moment μ. If the substance is placed in an applied magnetic field H, each spin can point either "up" (i.e., parallel to H) or "down." We denote the corresponding states by $+$ and $-$, respectively. The two possible energies of each nucleus are then

$$\epsilon_\pm = \mp \mu H \tag{15·3·1}$$

Let n_+ be the mean number of spins pointing up and n_- be the mean number of spins pointing down. Clearly, $n_+ + n_- = N$.

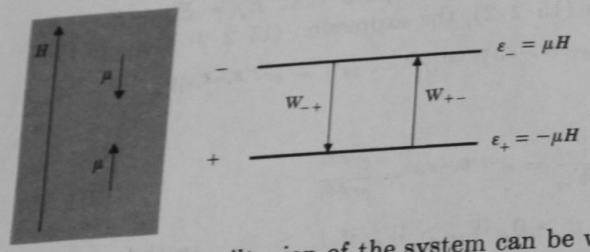

Fig. 15·3·1 Energy levels of a nucleus of spin ½ in an external magnetic field H. The magnetic moment μ is assumed to be positive in this diagram.

The total Hamiltonian of the system can be written as

$$\mathcal{H}^{(0)} = \mathcal{H}_n + \mathcal{H}_L + \mathcal{H}_i$$

Here $\mathcal{H}_n$ is the Hamiltonian expressing the interaction between the nuclear moments and the external field H; $\mathcal{H}_L$ is the Hamiltonian describing the "lattice," i.e., all non–spin degrees of freedom of the nuclei and all other atoms in the substance. The Hamiltonian $\mathcal{H}_i$ describes the interaction between the spins of the nuclei and the lattice, and causes transitions between the possible spin states of the nuclei. (For example, the magnetic moment of a *moving* nucleus produces a fluctuating magnetic field at the positions of other nuclei and this field causes transitions.) Let W_{+-} be the transition probability per unit time that a nucleus flips its spin from "up" to "down" as a result of interaction with the lattice. The lattice itself is a large system which can be regarded as being always very close to internal equilibrium at the absolute temperature $T = (k\beta)^{-1}$. Thus (15·2·10) allows one to write the relationship

$$\frac{W_{-+}}{W_{+-}} = \frac{e^{-\beta\epsilon_+}}{e^{-\beta\epsilon_-}} = e^{\beta(\epsilon_- - \epsilon_+)} \tag{15·3·2}$$

Now (15·3·1) gives $\beta(\epsilon_- - \epsilon_+) = 2\beta\mu H$. For nuclei the magnetic moment $\mu \approx 5 \cdot 10^{-24}$ ergs/gauss so that in laboratory fields of the order of $H = 10^4$ gauss

$$\beta\mu H = \frac{\mu H}{kT} \approx \frac{5 \cdot 10^{-4}}{T} \ll 1$$

for all but *exceedingly* low temperatures. Even for electronic moments, which are about 1000 times larger, this inequality is almost always well satisfied. By expanding the exponential, the relation (15·3·2) can then be written in the form

$$W_{+-} \equiv W$$

and

$$W_{-+} = W(1 + 2\beta\mu H), \qquad \text{where } \beta\mu H \ll 1 \tag{15·3·3}$$

Finally, there may also be present an externally applied alternating magnetic field of angular frequency ω. If $\hbar\omega \approx \epsilon_- - \epsilon_+ = 2\mu H$, this field will induce transitions between the spin states of a nucleus. (If $H \approx 10^4$ gauss, ω is typically a radio frequency (rf) of the order of 10^8 sec^{-1}.) Let w_{+-} be the transition probability per unit time for the "up" to "down" transition induced by this rf field. Then one again has the symmetry property (15·1·3)

$$w_{+-} = w_{-+} \equiv w \tag{15·3·4}$$

Here $w = w(\omega)$ is only appreciable if ω satisfies the resonance condition $\hbar\omega \approx 2\mu H$.

The master equations for $n_+(t)$ and $n_-(t)$ then become

$$\left.\begin{aligned} \frac{dn_+}{dt} &= n_-(W_{-+} + w) - n_+(W_{+-} + w) \\ \frac{dn_-}{dt} &= n_+(W_{+-} + w) - n_-(W_{-+} + w) \end{aligned}\right\} \tag{15·3·5}$$

By subtracting the second equation from the first, one obtains

$$\frac{d}{dt}(n_+ - n_-) = -2n_+(W_{+-} + w) + 2n_-(W_{-+} + w) \tag{15·3·6}$$

Introducing the population difference

$$n \equiv n_+ - n_- \tag{15·3·7}$$

and using (15·3·3), the relation (15·3·6) becomes

$$\frac{dn}{dt} = -2(W + w)n + 2\beta\mu HWN \tag{15·3·8}$$

Here we have put $4\beta\mu HWn_- = 4\beta\mu HW\left(\frac{1}{2}N - n\right) \approx 2\beta\mu HWN$, since one always has $n \ll N$ in the temperature range of interest.

Let us now investigate various cases of interest. Consider first the equilibrium situation in the absence of an applied rf field, i.e., with $w = 0$. Then $dn/dt = 0$, and (15·3·8) yields for the *equilibrium* excess number of spins

$$n_0 = N\beta\mu H \tag{15·3·9}$$

This is, of course, the result which follows from the canonical distribution according to which one has *in equilibrium*

$$n_\pm = N\frac{e^{\pm\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}} \approx N\frac{1 \pm \beta\mu H}{2} = \frac{1}{2}N(1 \pm \beta\mu H)$$

so that $n_0 = n_+ - n_-$ assumes the value (15·3·9)

Hence (15·3·8) can be written in the form

$$\frac{dn}{dt} = -2W(n - n_0) - 2wn \tag{15·3·10}$$

In the absence of a rf field when $w = 0$, this yields upon integration

$$n(t) = n_0 + [n(0) - n_0]\,e^{-2Wt} \tag{15·3·11}$$

where $n(0)$ is the population difference at the initial time $t = 0$. Thus $n(t)$ approaches its equilibrium value n_0 exponentially with a characteristic "relaxation time" $(2W)^{-1}$. Obviously, the larger the interaction W of the spins with the lattice heat reservoir, the shorter the relaxation time.

Suppose now that the interaction of the spins with the lattice is very weak,

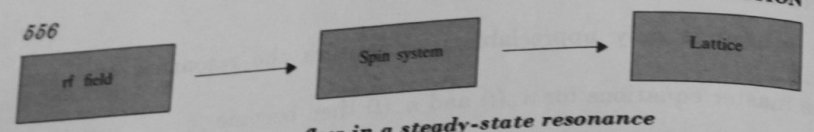

Fig. 15·3·2 Net energy flow in a steady-state resonance absorption experiment.

so that $W \approx 0$, and that a rf magnetic field is applied. Then (15·3·10) becomes

$$\frac{dn}{dt} = -2wn$$

so that

$$n(t) = n(0)\, e^{-2wt} \tag{15·3·12}$$

The population difference then becomes exponentially zero within a characteristic time $(2w)^{-1}$ which is inversely proportional to the strength of the interaction with the applied rf field. The reason for this is quite clear. Since there are more nuclei in the lower state of Fig. 15·3·1 than in the upper state, the transitions induced by the rf field result in a net absorption of power equal to $(n_+ - n_-)w(2\mu H)$. The nuclear spin system is essentially isolated since $W \approx 0$; hence the energy absorbed from the rf field goes to increase the energy and hence the "spin temperature T_s" of the spins until T_s approaches infinity. At this point $n_+ = n_-$, the population difference $n = 0$, and there is no further absorption of rf power. The spin system is then said to be "saturated."

If one *does* want to observe absorption of rf power in a steady state situation, there must be adequate contact between the spin system and the lattice heat reservoir. In that case the power absorbed by the spin system is in turn given off to the lattice (which, being a system of very large heat capacity, experiences only an infinitesimal increase in temperature). In the steady state $dn/dt = 0$ so that (15·3·10) becomes

$$W(n - n_0) = -wn$$

or

$$n = \frac{n_0}{1 + (w/W)} \tag{15·3·13}$$

Thus n is less than the equilibrium value n_0 by an amount which depends on the ratio w/W of the transition probabilities. If $w \ll W$, $n \to n_0$; but if $w \gg W$, $n \to 0$ and one gets saturation.

15·4 *Dynamic nuclear polarization; Overhauser effect*

Nonequilibrium methods for achieving nuclear polarization (the so-called "Overhauser effect" being one such method) provide a particularly illuminating illustration of the ideas presented in the last few sections. Consider a substance containing both nuclei of spin $\frac{1}{2}$ and magnetic moment μ_n, and also unpaired electrons of spin $\frac{1}{2}$ and magnetic moment μ_e ($\mu_e < 0$). The substance is placed in an external magnetic field H pointing in the z direction. Suppose

that the principal interaction of a nucleus is with an electron through "hyperfine interaction," i.e., through the magnetic field produced by the electron at the position of the nucleus. (This interaction is described by a Hamiltonian of the form $\mathcal{H}_{ne} = a\boldsymbol{I}\cdot\boldsymbol{S}$ where $\boldsymbol{I}$ is the nuclear and $\boldsymbol{S}$ the electronic spin angular momentum.) Since no z component of external torque acts on the system consisting of nucleus and electron (i.e., since the total Hamiltonian of this system is invariant under rotations about the z direction), the *total* z component of angular momentum $(I_z + S_z)$ of this system is a constant of the motion. Thus the transitions induced by the interaction between a nucleus and an electron must always be such that whenever the nucleus flips its spin from "up" to "down," the electron must flip its spin from "down" to "up," and vice versa. We shall denote the transition probability per unit time due to this interaction by $W_{ne}(+\,-\to-\,+)$ where $+$ and $-$ indicate up and down orientations of the nucleus n, and $+$ and $-$ up and down orientations of the electron e.

The nuclei interact then predominantly with the electron spins, which in turn interact appreciably with the lattice heat reservoir. It is through this chain of interactions that the nuclear spins attain the thermal equilibrium situation corresponding to the lattice temperature $T = (k\beta)^{-1}$. Let n_+ and n_- denote the mean number of nuclear "up" and "down" spins; let N_+ and N_- denote the mean number of electron "up" and "down" spins. In thermal equilibrium one then obtains, for the nuclei of energy $\epsilon_\pm = \mp\mu_n H$,

$$\frac{n_+}{n_-} = \frac{e^{\beta\mu_n H}}{e^{-\beta\mu_n H}} = e^{2\beta\mu_n H} \tag{15·4·1}$$

Also for the electrons of energy $E_\pm = \mp\mu_e H$,

$$\frac{N_+}{N_-} = \frac{e^{\beta\mu_e H}}{e^{-\beta\mu_e H}} = e^{2\beta\mu_e H} \tag{15·4·2}$$

The degree of polarization of the nuclei and electrons can be measured by the respective ratios defined by

$$\xi_n \equiv \frac{n_+ - n_-}{n_+ + n_-} \quad \text{and} \quad \xi_e \equiv \frac{N_+ - N_-}{N_+ + N_-} \tag{15·4·3}$$

Each ξ lies in the range $-1 \le \xi \le 1$. Since $|\mu_e| \approx 1000|\mu_n|$, it is clear by (15·4·1) and (15·4·2) that $\xi_n \ll \xi_e$. Even if one goes to such high applied fields H and low temperatures T that the electrons are appreciably polarized, the degree of nuclear polarization is thus still very small, in particular much too small to do nuclear physics experiments on polarized nuclei.

From the point of view of the transition probabilities one can regard the combined system $(n + e)$ of nucleus and electron as being in thermal contact with the lattice heat reservoir. It then follows by (15·2·10) that the transition probabilities must satisfy the relation

$$\frac{W_{ne}(+\,-\to-\,+)}{W_{ne}(-\,+\to+\,-)} = e^{-\beta(\epsilon_- + E_+ - \epsilon_+ - E_-)} = e^{-2\beta(\mu_n - \mu_e)H} \tag{15·4·4}$$