

Principle of Detailed Balance*

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This note answers a question raised by Lloyd and Pake as to whether or not the principle of detailed balance applies in nonequilibrium steady states. It is shown that detailed balance holds only at equilibrium, and that nonequilibrium steady states must be maintained by cyclic processes.

THE principle of detailed balance requires that transitions between any two states take place with equal frequency in either direction at equilibrium.¹ This principle prevents the maintenance of equilibrium by means of cyclic processes. In a recent paper Lloyd and Pake² have raised the question as to whether or not detailed balance applies to nonequilibrium steady states. Their discussion suggested a negative answer, and it is the purpose of this note to discuss the problem further. Our conclusion is that detailed balance applies only at equilibrium, and that cyclic processes are essential for the maintenance of nonequilibrium steady states.

We shall consider a very simple example, the one treated by Lloyd and Pake, though the nature of the argument is not limited to this case. We consider a system with three energy states ϵ_i , ($i=1,2,3$). Let p_i denote the probability that the system (considered as one member of an ensemble) is in state i . We have, of course, the restriction

$$\sum_i p_i = 1. \quad (1)$$

The time variation of the p_i is determined by the equations

$$d p_i / dt = \sum_j' (a_{ji} p_j - a_{ij} p_i), \quad (2)$$

where the prime indicates that the term $j=i$ is omitted from the summation. The quantity a_{ij} represents the probability per unit time of a transition from state i to state j . We assume that our system is maintained at temperature T by thermal contact with a heat bath at this temperature. It follows³ that the a_{ij} satisfy the equations

$$a_{ij} \exp(-\epsilon_i/kT) = a_{ji} \exp(-\epsilon_j/kT). \quad (3)$$

In the absence of any external influence on the system, there is only one steady state solution of Eq.

(2), the equilibrium state in which $p_i^0 = c \exp(-\epsilon_i/kT)$, c being a constant. Because of Eq. (3), it is evident that the principle of detailed balance holds in equilibrium, $a_{ij} p_j^0 = a_{ji} p_i^0$.

We now subject the system to an external influence which causes transitions between states 1 and 2, so that Eq. (2) becomes

$$\begin{aligned} d p_1 / dt &= \sum_j' (a_{j1} p_j - a_{1j} p_1) + b(p_2 - p_1) \\ d p_2 / dt &= \sum_j' (a_{j2} p_j - a_{2j} p_2) + b(p_1 - p_2) \\ d p_3 / dt &= \sum_j' (a_{j3} p_j - a_{3j} p_3). \end{aligned} \quad (4)$$

Here b is the induced transition probability per unit time for transitions in either direction between states 1 and 2. (In the experimental situation treated by Lloyd and Pake the system is a set of spins and the transitions are induced by an oscillating magnetic field of frequency $\nu = (\epsilon_2 - \epsilon_1)/h$.)

To determine the steady state it is necessary to solve Eq. (4) with all $d p_i / dt$ equal to zero, using the constraint expressed by Eq. (1). Our interest is not in the solutions $p_i^{(s)}$, but rather in the rates of transition which exist in the steady state. Carrying out the algebra we readily obtain the following results⁴:

$$\begin{aligned} a_{31} p_3^{(s)} - a_{13} p_1^{(s)} &= (a_{12} + b) p_1^{(s)} - (a_{21} + b) p_2^{(s)} \\ &= a_{23} p_2^{(s)} - a_{32} p_3^{(s)} = b a_{13} a_{32} [\exp\{(\epsilon_2 - \epsilon_1)/kT\} - 1]. \end{aligned} \quad (5)$$

It is clear from Eq. (5) that detailed balance does *not* apply to the steady state considered here. This state is in fact maintained by a cyclic process which we may indicate schematically as $3 \rightarrow 1 \rightarrow 2 \rightarrow 3$, where the arrows indicate a net "flow." (We assume here that $\epsilon_2 > \epsilon_1$, otherwise all arrows are reversed.) As might be expected the net rate of induced transitions between states 1 and 2, corresponds to an absorption of energy by the system from the external source. We have

$$\begin{aligned} b(p_1^{(s)} - p_2^{(s)}) &= b a_{13} a_{32} [\exp\{(\epsilon_2 - \epsilon_1)/kT\} - 1] \\ &\quad + b a_{21} (a_{31} + a_{32}) [1 - \exp\{-(\epsilon_2 - \epsilon_1)/kT\}], \end{aligned} \quad (6)$$

where the second term is equal to $a_{21} p_2^{(s)} - a_{12} p_1^{(s)}$, the net rate of "natural" transitions in the reverse direction.

We can understand the necessity for the cycle of transitions $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ which maintains the steady

⁴ A constant factor equal to Δ^{-1} , where Δ is the determinant of coefficients in Eq. (4), has been omitted from the right-hand sides Eqs. (5), (6).

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¹ See Richard C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, Oxford, 1938), pp. 165, 521. See also L. Onsager, *Phys. Rev.* **37**, 405 (1931); **38**, 2265 (1931). The principle is thoroughly discussed in J. S. Thomsen, *Phys. Rev.* **91**, 1263 (1953).

² J. P. Lloyd and G. E. Pake, *Phys. Rev.* **94**, 579 (1954), Secs. 3-5.

³ This relationship is mentioned in reference 2. For a general derivation, see M. J. Klein and P. H. E. Meijer, *Phys. Rev.* **96**, 250 (1954), Appendix. An alternate derivation can be found in R. T. Cox, *Revs. Modern Phys.* **22**, 238 (1950), Sec. 2. (The author would like to thank Dr. J. S. Thomsen for pointing out this reference.)

state by studying the rate of entropy production in this state. It is clear that entropy is produced since the energy absorbed from the external source is converted into thermal energy of the heat bath.

We can write,⁵ for the total rate of entropy production,

$$\frac{dS}{dt} = -k \left[\sum_i \frac{dp_i}{dt} \log p_i + \sum_i \frac{\epsilon_i}{kT} \sum_j (a_{ji} p_j - a_{ij} p_i) \right]. \quad (7)$$

The first term comes from the redistribution over the states i and vanishes in the steady state. The second term arises from the energy delivered to the heat bath at temperature T . Making use of Eq. (4) and of the fact that all dp_i/dt vanish in the steady state, we can write the rate of entropy production in the form

$$dS/dt = b(p_1^{(s)} - p_2^{(s)})(\epsilon_2 - \epsilon_1)(1/T). \quad (8)$$

⁵ The expression for the rate of entropy production can be derived by the method used in M. J. Klein and P. H. E. Meijer, *Phys. Rev.* **96**, 250 (1954), Sec. III. It can be proved that the steady state solution of Eq. (4) is the state of minimum entropy production as in the above reference. This point will be discussed further in a paper now in preparation.

The first factor, $b(p_1^{(s)} - p_2^{(s)})(\epsilon_2 - \epsilon_1)$, is the rate at which energy is absorbed from the external source, and the factor $(1/T)$ arises from the transfer of this energy to the heat bath at temperature T .

Now the rate of entropy production can also be expressed in terms of the energy delivered to the heat bath per unit time as

$$dS/dt = (\epsilon_2 - \epsilon_1)(1/T) [(a_{21} p_2^{(s)} - a_{12} p_1^{(s)}) + (a_{31} p_3^{(s)} - a_{13} p_1^{(s)})] + (\epsilon_3 - \epsilon_2)(1/T) \cdot [(a_{32} p_3^{(s)} - a_{23} p_2^{(s)}) + (a_{31} p_3^{(s)} - a_{13} p_1^{(s)})], \quad (9)$$

where we have written $(\epsilon_3 - \epsilon_1) = (\epsilon_3 - \epsilon_2) + (\epsilon_2 - \epsilon_1)$. It is seen from the foregoing analysis, particularly Eqs. (5) and (6), that these two expressions, Eqs. (8) and (9), agree precisely because of the failure of the principle of detailed balance and because of the existence of a cycle of transitions.

In conclusion, we may state that the argument carried out above for a special example should apply quite generally: the principle of detailed balance cannot hold in nonequilibrium steady states.

Ultrasonic Propagation in Magnetically Cooled Helium*†

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Measurements have been made of the velocity and attenuation of ordinary sound in liquid helium at a frequency of 12.1 Mc/sec, over the temperature range from 1°K down to 0.1°K. The velocity is essentially independent of temperature and has the value 240 ± 5 m/sec. The attenuation passes through two closely spaced maxima near 0.9°K and then falls smoothly to zero as the absolute zero is approached. These results agree qualitatively with the theoretical predictions of Khalatnikov.

I. INTRODUCTION

THE present paper describes a series of experiments on the propagation of ordinary ("first") sound in liquid helium below 1°K. Interest in these measurements was first stimulated by the experiments performed by one of the authors¹⁻² in the range of temperatures obtainable by pumping on the helium bath and by the theoretical calculations of Khalatnikov.³⁻⁵

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† Preliminary results have been reported in a recent Letter by the authors [*Phys. Rev.* **95**, 565 (1954)].

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¹ K. R. Atkins and C. E. Chase, *Proc. Phys. Soc. (London)* **A64**, 826 (1951).

² C. E. Chase, *Proc. Roy. Soc. (London)* **A220**, 116 (1953).

³ I. M. Khalatnikov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **20**, 243 (1950).

⁴ I. M. Khalatnikov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **23**, 8 (1952).

⁵ I. M. Khalatnikov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **23**, 21 (1952).

These measurements showed that the velocity of propagation u_1 levels off to an almost constant value at temperatures somewhat above 1°K, but that the attenuation passes through a maximum just below 1°K and exhibits the frequency dependence, over the range from 2 Mc/sec to 12 Mc/sec, characteristic of a relaxation process. This behavior was predicted by Khalatnikov. It was therefore decided to extend the measurements into the temperature range obtainable by the adiabatic demagnetization of a paramagnetic salt, focusing attention chiefly upon the attenuation. These experiments were performed under the saturated vapor pressure at a frequency of 12.1 Mc/sec, and extend from about 1°K to 0.1°K.

II. EXPERIMENTAL METHOD

1. Demagnetization Cryostat

The cryostat in which the experiments were performed is shown schematically in Fig. 1. This apparatus is essentially the same as one originally designed by Dr.