Microscopic Reversibility and Detailed Balance

An overview

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In a number of recent textbooks and articles on non-equilibrium statistical mechanics, the concepts of microscopic reversibility and detailed balance are used either inconsistently or inaccurately. DeGroot and Mazur (1) use the terms interchangeably and generally in pairs. Onsager (2) equates the term, dynamical reversibility, with microscopic reversibility, while Morowitz (3) utilizes the terms dynamical reversibility and detailed balance synonymously. Some physical chemistry textbooks erroneously use detailed balance to describe microscopic reversibility or claim that the law of mass action follows from detailed balance (4, 5). Introduced in this manner, the concepts not only add little to the understanding of chemical kinetics, but also lead to a confusion between the macroscopic and microscopic descriptions of a changing chemical system. Carefully developed, microscopic reversibility and detailed balance provide keen insights into non-equilibrium processes.

In this article, we will present a heuristic development of microscopic reversibility and detailed balance and establish their relationship. It is apparent that both semantic and actual inconsistencies exist in the application of these concepts. Microscopic reversibility and detailed balance are not equivalent, although at equilibrium they may appear so. After tracing the evolution of these ideas at equilibrium, we shall consider a simple non-equilibrium process, e.g. one dimensional heat flow, to sharpen the distinction between the two terms. By extending Tolman's original definition, we can consider how exclusion principles (like the Second Law) arise in science and why they are utilized.

An understanding of microscopic reversibility and detailed balance begins with a consideration of the term "reversible." In thermodynamics, reversibility implies the ability to control the direction of a process by infinitesimal changes in the external forces. In mechanics, reversibility implies that the appropriate equations describing a process are invariant to the transformation of $t \rightarrow -t$ and $v \rightarrow -v$ (time reversal operator). Equivalently we may speak of reversing the sign of either the time or motion variable with the consequence that the trajectory of the system retraces itself. The significant point is that the reversibility of thermodynamics and that of mechanics are equally abstract and hypothetical. One can no more instantly reverse the direction of change of any real system having inertia (even with the use of an infinitely large force) than he can reverse the direction of time. The concept of reversibility is primarily useful in analyzing processes of change.

As a result of his work rationalizing the use of reversible mechanical equations to describe the phenomenological irreversibility of fluid behavior (H-Theorem), Tolman (6) formulated the concepts of microscopic reversibility and detailed balance. Faced with Boltzmann's identification of the equilibrium condition with the most probable distribution, and the ergodic hypothesis requiring a cycling through all possible states, Tolman reasoned that direct interconversions between various cells making up the

state space defining the system would satisfy both conditions. Microscopic reversibility represents his conclusion that under equilibrium conditions, molecular processes and their reverses occur at the same rate. This principle of equal frequency for reverse molecular processes obviously ensures the persistence of the equilibrium distribution. More generally, the equilibrium distribution can be maintained by a balancing of the number of particles or systems moving into and out of the various regions of the appropriate state space. Tolman refers to this concept as the principle of detailed balance.

For the case of the microcanonical ensemble where states are defined by values of number, volume, and energy, microscopic reversibility is given by eqn. (1) where τ_{ij} is the probability

$$\tau_{ij} = \tau_{ji} \tag{1}$$

of a transition from state i to state j. Similarly, detailed balance can be expressed as

$$f_i \tau_{ij} = f_j \tau_{ji} \tag{2}$$

where f_i is the number of particles or systems in state i and τ_{ij} is again the transition probability. Equation (2) can be generalized to cover situations necessitating the use of the canonical ensemble (7). Realizing that the extremely small magnitude of the fluctuations in energy about the average renders the canonical ensemble virtually equivalent to the microcanonical ensemble, the following discussion utilizing eqns. (1) and (2) would also apply to the more general case.

A two-dimensional kinetic model devised originally by the Ehrenfests (8) and modified slightly by ter Haar (9) clearly illustrates the concepts of microscopic reversibility and detailed balance and establishes their relationship to chemical kinetics (see also, Starzak (12)).

Picture, as in Figure 1, a number of square particles, the Q-molecules, distributed at random in the x,y-plane with sides of length L and diagonals parallel to the x- and y-axes. The average surface density of the Q-molecules is N_q, and it is low enough so that their average separation
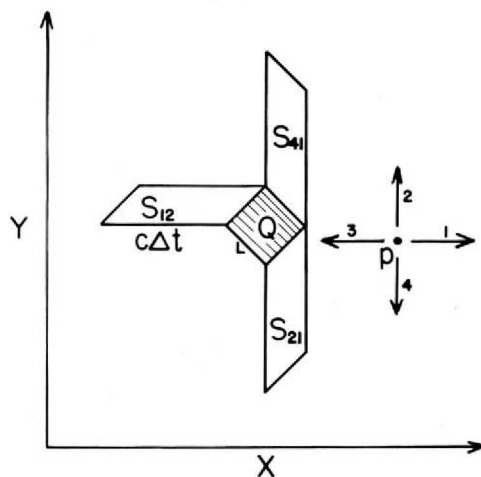

Figure 1. Two-dimensional kinetic model illustrating the interchange among velocity classes.

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is large compared to L. Into this system we introduce a large number of non-interacting point particles with density N_p, the P-molecules, which collide elastically with the Q-molecules. These P-molecules are injected in such a way that their trajectories are restricted to the positive x (here defined as direction one), positive y (direction two), negative x (direction three), and negative y (direction four). Initially all the P-molecules have a speed c and f_1, f_2, f_3, and f_4 give the number of particles moving in each of the four directions.

Now consider the process of the change of direction of the P-molecules and the resultant evolution of the distribution of velocities f_i. The number of P-molecules changing from direction i to j per unit time is given by

$$N_{ij} = \frac{f_i S_{ij} N_q}{\Delta t} \quad (3)$$

where S_{ij} is the area of a parallelogram of length $c\Delta t$ and altitude $L\sqrt{2}/2$ (i.e. the collision cross-section per Q-molecule for change from direction i to j). If we define a transition probability

$$\tau_{ij} = \frac{S_{ij} N_q}{\Delta t} \quad (4)$$

and note that in this example all the τ_{ij} are equal, we may write the equations of change for the distribution functions

$$\frac{df_1}{dt} = \tau[f_2 + f_4 - 2f_1]$$

$$\frac{df_2}{dt} = \tau[f_3 + f_1 - 2f_2]$$

$$\frac{df_3}{dt} = \tau[f_4 + f_2 - 2f_3] \quad (5)$$

$$\frac{df_4}{dt} = \tau[f_1 + f_3 - 2f_4]$$

By combining these equations to get

$$\frac{d}{dt}[(f_1 - f_3)] = -2\tau[f_1 - f_3]$$

$$\frac{d}{dt}[(f_2 - f_4)] = -2\tau[f_2 - f_4] \quad (6)$$

$$\frac{d}{dt}[(f_1 + f_3) - (f_2 + f_4)] = -4\tau[(f_1 + f_3) - (f_2 + f_4)]$$

and using the fact that at equilibrium the time derivatives go to zero, one finds that

$$f_1 = f_2 = f_3 = f_4 = 1/4 N_p \quad (7)$$

Hence, at equilibrium, we find that

$$N_{ij} = N_{ji} \quad (8)$$

for this simple model.

This development of detailed balance is of course more general than our simple derivation would imply. Suppose, for instance, that the Q-molecules are irregular quadrilaterals. Clearly S_{ij} is no longer equal to S_{ji}. However, since the Q-molecules would also be positioned randomly in any physical system (no Maxwellian Demons intervening), the transition probability would be some average of the S_{ij} and equal for the conversion of all directional states. In this respect, microscopic reversibility is an expression of our ignorance on the molecular scale. Another way to see this is to consider a single molecule in a one-dimensional box with reflecting walls. Not knowing where the molecule is in the box means that in any time interval there is an equal probability of the molecule changing directions from left to right or vice versa. It should be pointed out, however, that the usual derivation of the principle of microscopic reversibility proceeds in a different direction. By

definition, at equilibrium the number of transitions between the various cells of state space and the number of states per cell are equal. It immediately follows that the probability of the transitions between two such cells is the same at equilibrium.

As we have noted, one of the common uses of the principle of detailed balance is the justification of the phenomenological equations of chemical kinetics. The argument is one which always alludes to the similar forms of the equations, namely that some rate is equal to the product of a constant and some concentration. The obvious consideration that the rate constant is a macroscopic parameter, while the transition probability is a microscopic concept, is usually overlooked with a resultant confusion between the two levels of description.

The depth of this confusion is evident if we consider the unimolecular reaction of A $\rightleftarrows$ B. At equilibrium, [A] $\neq$ [B] unless the equilibrium constant fortuitously equals one. Note from eqn. (2), however, that since $\tau_{ij} = \tau_{ji}$, $f_i = f_j$ whenever detailed balance holds. If the mass action-detailed balance analogy were valid, [A] would always equal [B]. This contradiction is easily resolved by the realization that the identity $f_i = f_j$ actually implies that the number of states of the A molecules is equal to the number of states for the B molecules. This equal measure or range in the statistical mechanical state space describing the A, B system does not mean [A] = [B] since the number of possible transitions between the various states of A and B determines the rate constants. In fact, the rate constant $k_{A\rightarrow B}$ is given by

$$k_{A \rightarrow B} = \sum_{\substack{\text{states} \\ \text{of A}}} \tau_{A, B} \quad (9)$$

It is apparent that detailed balance can only obtain at equilibrium, for otherwise chemical change would not occur. Tolman *(6)*, by using a derivation based on the constancy of measure in the various regions of state space, is forced to restrict the equality expressed by microscopic reversibility to equilibrium situations. It is important to note, however, that microscopic reversibility also holds for non-equilibrium processes. This essential feature is evident when considerations of time reversal invariance are used to develop microscopic reversibility.

Consider a macroscopic state X_i defined by known values of number, volume, and energy which evolves to some state X_j. Whether we view X_i changing as a result of ergodic considerations or modifications in the external forces on the system, there is a certain probability τ_{ij} that X_i will evolve to X_j in some time dt. The method of statistical mechanics requires that we postulate a set of microscopic states, $\{s\}$, with coordinates of position and momentum which are accessible to X_i. By following the motion of set $\{s\}$ as it evolves to set $\{s'\}$ using either Newtonian or quantum mechanics, and then carrying out the appropriate averaging procedure over the set $\{s'\}$, we will be able to predict X_j, something which was impossible to do directly. It is clear from our discussion of reversibility that the equations of both Newtonian and quantum mechanics are invariant under the time reversal operator. Further, for each state s_n' in set $\{s'\}$, we must recognize the occurrence of a second state s_{nr}', which is accessible to X_j and which differs from s_n' only in having reversed momenta coordinates. The solution of the dynamical equations shows that while some state s_n is evolving to s_n' in time dt, state s_{nr}' is changing to s_{nr} in time $-dt$. It follows that the transition probabilities $s_n \rightarrow s_n'$ and $s_{nr}' \rightarrow s_{nr}$ are the same. All we need do to obtain microscopic reversibility, $\tau_{ij} = \tau_{ji}$, in the macroscopic state space is to realize that a microscopic state and its reverse correspond to the same macroscopic state since the energy coordinate depends on the square of the momenta. Since we have no reason to believe that the present dynamical equations do
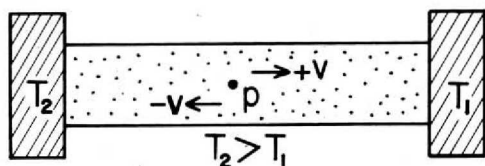
Figure 2. Paradox of "irreversible thermodynamics" when applied to steady state conductive heat flow.

Figure 3. Mechanical analog of heat flow paradox.

not apply equally to the description of non-equilibrium processes, we have established microscopic reversibility with no reference to an equilibrium condition.

The fact that microscopic reversibility holds for non-equilibrium processes can lead to interesting paradoxes. Consider the problem of steady state conductive heat flux through a one-dimensional box containing a rarefied gas. Wall temperatures will be held at T_1 and T_2 as shown in Figure 2. The application of "irreversible thermodynamics" to this situation would require the assumption of local equilibrium so that one could formulate the rate of entropy production. Alternatively, one could apply the method of statistical mechanics with its concomitant principle of microscopic reversibility. In either case, the direct application of theory predicts that a particle at any position in the box has an equal probability of having a positive or negative velocity. Conduction of heat in one direction is thus countered by transitions in the other with the result that no heat flows despite the temperature gradient. We know from experience, however, that control of the profiles of number, velocity, and temperature yields a predictable and reproducible heat flux. Unfortunately, the most probable distribution corresponding to these properties is the equilibrium, Maxwellian distribution, which yields a zero-valued heat flux. The only means of logically countering this paradox is to make use of some additional information and exclude a portion of the conceivable set of dynamically accessible states. In the process of devising a model and constructing a theory, we have envisioned too many states.

A simple analogy to the heat flow problem is the motion of a ball on a pivoting plane as shown in Figure 3, (a) and (b). Having only a photograph of the system and no details of the motion, as is always the case for individual molecules, we are forced to conclude that the ball in Figure 3 (a) may be rolling either up or down the incline. There is, however, a very general piece of information which can determine the direction of motion, namely, whether or not the system was recently at equilibrium. Knowledge that equilibrium existed just prior to the photograph of Figure 3 (a), as in Figure 3 (b), means the ball is very probably rolling down the incline. Barring the intervention of a Maxwellian Demon, recent equilibrium in the system permits us to exclude one of the two possible states and establish the direction of change.

The application of exclusion principles is of course common in science. The possibility that a gas uniformly distributed throughout a box will spontaneously withdraw to its initial state of being trapped in a corner is denied by the Second Law. This is despite the guarantee of the Poincaré recurrence theorem that the system will return arbitrarily close to its initial state in a finite time. Consider also Caratheodory's statement of the Second Law (10) which rules out the possibility of reaching certain states from any arbitrary state by an adiabatic process.
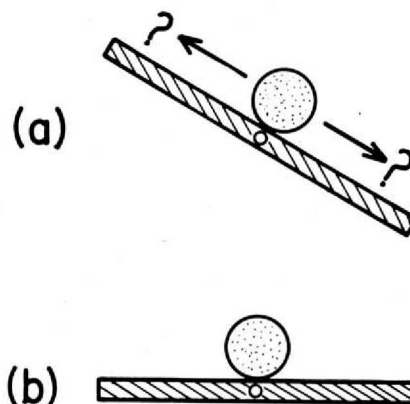
The unique feature of all exclusion principles is a reduction in the number of states accessible to a system in such a way that a directionality is established for the process considered. Very generally, then, the resolution of our zero heat flow paradox is to exclude a portion of the set of dynamically accessible states. One possible way to do this would be to utilize the historical information implicit in the nearness in time of the system to a recent equilibrium condition. For the equally likely states we would choose those which were accessible at the time the temperature gradient was impressed, or have evolved from these initially accessible states. With this exclusion of states, we can use statistical mechanics (kinetic theory) to predict the desired heat flux (11).

In summary, although microscopic reversibility and detailed balance are closely related, their applicability is quite different. Microscopic reversibility is necessary for detailed balance and follows from the reversibility inherent in the dynamical description of the particle model. Detailed balance, which holds only at equilibrium, is of use in the calculation of rates of processes in one direction from rates in the opposite direction. Both concepts can be an aid in the teaching of chemical kinetics, but only if care is taken not to confuse the microscopic and macroscopic descriptions of reality.

Acknowledgment

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