

For a large system* (in thermal contact with another large system) there will never occur spontaneously significant differences between the actual value of the entropy and the value of the entropy of the most probable configuration of the system. We showed this for the model spin system in the argument following (17); we used "never" in the sense of not once in the entire age of the universe, 10^{18} s. We can only find a significant difference between the actual entropy and the entropy of the most probable configuration of the macroscopic system very shortly after we have changed the nature of the contact between two systems, which implies that we had prepared the system initially in some special way. Special preparation could consist of lining up all the spins in one system parallel to one another or collecting all the molecules in the air of the room into the system formed by a small volume in one corner of the room. Such extreme situations never arise naturally in systems left undisturbed, but arise from artificial operations performed on the system.

Consider the gas in a room: the gas in one half of the room might be prepared initially with a low value of the average energy per molecule, while the gas in the other half of the room might be prepared initially with a higher value of the average energy per molecule. If the gas in the two halves is now allowed to interact by removal of a partition, the gas molecules will come very quickly† to a most probable configuration in which the molecules in both halves of the room have the same average energy. Nothing else will ever be observed to happen. We will never observe the system to leave the most probable configuration and reappear later in the initial specially prepared configuration. This is true even though the equations of motion of physics are reversible in time and do not distinguish past and future.

LAWS OF THERMODYNAMICS

When thermodynamics is studied as a nonstatistical subject, four postulates are introduced. These postulates are called the laws of thermodynamics. In essence, these laws are contained within our statistical formulation of thermal physics, but it is useful to exhibit them as separate statements.

Zeroth law. If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other. This law is a consequence

* A large or macroscopic system may be taken to be one with more than 10^{10} or 10^{15} atoms.

† The calculation of the time required for the process is largely a problem in hydrodynamics.