

12.1: Mechanical Processes

When we talk about a purely mechanical process, we have in mind a system in which one or more unchanging objects can move relative to some reference frame. Their movements are described completely by Newton's laws of motion. The objects are characterized by their masses, locations, velocities, and accelerations. They may be subject to the effects of force fields, whose magnitudes can vary with location and time. We stipulate that the volume, pressure, temperature, entropy, composition, and the internal energy, U , of an individual object remain constant. Since entropy and volume are extensive state functions, we can obtain the entropy and volume of the objects in aggregate by summing up those for the individual objects. Moreover, the total entropy and the total volume are constants.

The energy of a purely mechanical system is the sum of its internal energy, U , its kinetic energy, τ , and its mechanical potential energy, v ; that is,

$$E = U + \tau + v.$$

U is the sum of the internal energies of the unchanging constituent objects. Since it is constant, the internal energy can be given an arbitrary value that we usually choose to be zero. When we do so, the energy of the system becomes the sum of its kinetic and potential energies. Noting explicitly that the entropy and volume are constant, we have

$$(\Delta E)_{SV} = \tau + v.$$

The essential distinction between a purely mechanical system and a thermodynamic system is that our models for mechanical systems focus on the motions of unchanging objects; our models for thermodynamic systems focus on the internal changes of stationary objects.

An important aspect of this distinction is that our definitions of equilibrium, reversibility, and spontaneous change in mechanical systems are not wholly congruent with the definitions we use in developing the principles of thermodynamics. Thus, an equilibrium state of a mechanical system is one in which the objects comprising the system are stationary with respect to some reference frame. For a mechanical system at equilibrium, the kinetic energy is constant and can usually be taken to be zero, $\tau = 0$. The motion of a system generally has no bearing on whether the substances that comprise the system are at equilibrium in a thermodynamic sense.

We normally consider that a sufficient condition for a mechanical system to be reversible is that—following some excursion to other states—the initial conditions of both the system and the surroundings can be restored exactly¹. In our thermodynamic view of reversibility, this condition is necessary but not sufficient: We say that a thermodynamic system is reversible only if the direction in which it is changing can be reversed at any time by an arbitrarily small change in its interaction with its surroundings. The initial conditions can be restored after any excursion.

Our treatments of the frictionless harmonic oscillator illustrate this imperfect congruence. Viewed as a mechanical system, a frictionless harmonic oscillator is a reversible system. If we adopt the view that it is continuously undergoing spontaneous change, our thermodynamic principles mean that its entropy is continuously increasing. However, since its state and that of its surroundings reproduce themselves exactly after every period of oscillation, our thermodynamic principles mean also that there is zero net change in the entropy over any complete oscillation. Clearly, this is a contradiction. If we attempt to salvage the situation by supposing that the entropy of an isolated freely moving harmonic oscillator is constant, our thermodynamic principles require us to say that it is at equilibrium. This contradicts the view that a mechanical system is at equilibrium only if its kinetic energy is zero. Since neither formulation is satisfactory, we recognize that we cannot expect to describe every mechanical system in purely thermodynamic terms.

Nor can we expect to describe every thermodynamic system in mechanical terms. This becomes obvious when we observe that the second law of thermodynamics is essential to our description of thermodynamic systems, but it is not among the principles of mechanics. Beginning in Chapter 20, we find that we can model the thermodynamic properties of a system that is itself a collection of a large number of subsystems by focusing on the average values of the properties of the subsystems. The laws of motion model the movements of the individual particles of a system. The laws of thermodynamics model the average properties of the particles in a system that contains a very large number of particles. While we cannot usefully describe an individual harmonic oscillator as a thermodynamic system, we see in §22-6 that the thermodynamic properties of a system composed of many identical harmonic oscillators can be modeled very successfully.

In short, mechanics and thermodynamics model different kinds of systems from fundamentally different perspectives. Nevertheless, when we limit our consideration of mechanical systems to the prediction of spontaneous change from one equilibrium state to

another, we can recognize that the criteria we are accustomed to apply to mechanical systems are analogous to our thermodynamic criteria as they apply to such processes.

From our thermodynamic perspective, a purely mechanical process involves no change in the entropy or volume of the system, and the criterion for irreversible change is $(\Delta E)_{SV} < w_{npv}$. From our mechanical perspective, an irreversible transition between equilibrium states is one in which various objects interact with one another or with various force fields. We consider that the process can occur if the change in the potential energy of the system is less than the work done on it; that is $\Delta v < w_{npv}$. In the mechanical system, some of the work done on the system is dissipated by frictional forces as heat that appears in the surroundings. (If the process involves no exchange of work with the surroundings, the criterion becomes $\Delta v < 0$.) If the mechanical system begins and ends at rest, we have $(\Delta E)_{SV} < \Delta v$, so that again $(\Delta E)_{SV} < w_{npv}$.

If no work is exchanged with the surroundings, potential energy minimization, $\Delta v < 0$, is a sufficient condition for spontaneous change to be possible in mechanical systems under the circumscribed conditions we have outlined. In Section 14-2, we find that minimization of the chemical potential energy,

$$\sum_{j=1}^{\omega} \mu_j dn_j < 0$$

is a necessary and sufficient condition for spontaneous change to be possible in a thermodynamic system. These conditions are parallel, but they are not equivalent to one another.

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