9.5: The Tiling Theorem and the Paths of Cyclic Process in Other Spaces

We view the tiling theorem as a generalization from experience, just as the machine-based statement of the second law is such a generalization. Let us consider the kinds of familiar observations from which we infer that every equilibrium state of any system is intersected by one and only one adiabat and by one and only one isotherm.

When only pressure–volume work is possible, each pressure–volume point specifies a unique equilibrium state of the system. Since temperature is a state function, the temperature of this state has one and only one value. When another form of work is possible, every $\mathit{\Phi}_i - \theta_i$ point specifies a unique state for which the temperature has one and only one value. From experience, we know that we can produce a new state of the system, at the same temperature, by exchanging heat and work with it in a concerted fashion. We can make this change of state arbitrarily small, so that successive equilibrium states with the same temperature are arbitrarily close to one another. This succession of arbitrarily close equilibrium states is an isotherm. Therefore, at least one isotherm intersects any equilibrium state. There cannot be two such isotherms. If there were two isotherms, the system would have two temperatures, violating the principle that temperature is a state function.

In an adiabatic process, the system exchanges energy as work but not as heat. From experience, we know that we can effect such a change with any reversible system. The result is a new equilibrium state. When we make the increment of work arbitrarily small, the new equilibrium state is arbitrarily close to the original state. Successive exchanges of arbitrarily small work increments produce successive equilibrium states that are arbitrarily close to one another. This succession of arbitrarily close equilibrium states is an adiabat.

If the same state of a system could be reached by two reversible adiabats involving the same form of work, the effect of doing a given amount of this work on an equilibrium system would not be unique. From the same initial state, two reversible adiabatic experiments could do the same amount of the same kind of work and reach different final states of the system. For example, in two different experiments, we could raise a weight reversibly from the same initial elevation, do the same amount of work in each experiment, and find that the final elevation of the weight is different. Any such outcome conflicts with the observations that underlie our ideas about reversible processes.

More specifically, the existence of two adiabats through a given point, in any $\mathit{\Phi}_i - \theta_i$ space, violates the machine-based statement of the second law. Two such adiabats would necessarily intersect a common isotherm. A path along one adiabat, the isotherm, and the second adiabat would be a cycle that restored the system to its original state. This path would enclose a finite area. Traversed in the appropriate direction, the cycle would produce work in the surroundings. By the first law, the system would then accept heat as it traverses the isotherm. The system would exchange heat with surroundings at a single temperature and produce positive work in the surroundings, thus violating the machine-based statement.

If an adiabatic process that connects two states A and B is reversible, we see that the system follows the same path, in opposite directions, when it does work going from A to B as it does when work is done on it as it goes from B to A.

From another perspective, we can say that the tiling theorem is a consequence of our assumptions about reversible processes. Our conception of a reversible process is that the energy, pressure, temperature, and volume are continuous functions of state, with continuous derivatives. That there is one and only one isotherm for every state is equivalent to the assumption that temperature is a continuous (single-valued) function of the state of the system. That there is one and only one adiabat for every state is equivalent to the assumption that $\left(\partial E/\partial V\right)_{T,\theta_1}$, or generally, $\left(\partial E/\partial \theta_i\right)_{T,V,\theta_{m\neq i}}$, is a continuous, single-valued function of the state of the system.

With these ideas in mind, let us now observe that any reversible cycle can be described by a closed path in a space whose coordinates are T and q^{rev}/T (entropy). In Figure 5, we sketch this space with q^{rev}/T on the abscissa; then an isotherm is a horizontal line, and line of constant entropy (an ***isentrope***) is vertical. A reversible Carnot cycle is a closed rectangle, and the area of this rectangle corresponds to the reversible work done by the system on its surroundings in one cycle. Any equilibrium state of the system corresponds to a particular point in this space. Any closed path can be tiled arbitrarily densely by isotherms and isentropes. Any reversible cycle involving any form of work is represented by a closed path in this space. Figure 5 is an alternative illustration of the argument that we make in Section 9.4. The path in this space is independent of the kind of work done, reinforcing the conclusion that $\oint dq^{rev}/T=0$ for a reversible Carnot cycle producing any form of work. The fact that a cyclic process corresponds to a closed path in this space is equivalent to the fact that entropy is a state function.

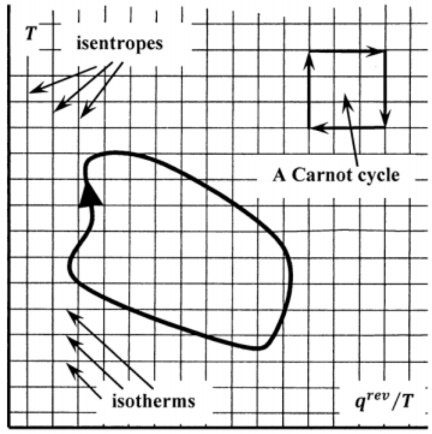

Figure 5. A reversible cycle described using coordinates T and q^{rev}/T.

To appreciate this aspect of the path of a cyclic process in $T - q^{rev}/T$ space, let us describe the path of the same process in a space whose coordinates are T and q^{rev}. With q^{rev} on the abscissa, isotherms are again horizontal lines and adiabats are vertical lines. In this space, a reversible Carnot cycle does not begin and end at the same point. The path is not closed. Similarly, the representation of an arbitrary reversible cycle is not a closed figure. See Figure 6. The difference between the representations of a reversible cyclic process in these two spaces illustrates graphically the fact that entropy is a state function while heat is not.

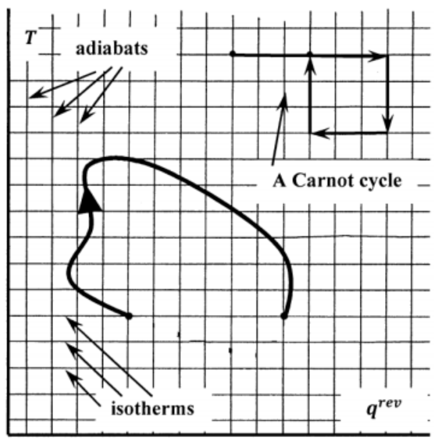

Figure 6. A reversible cycle described using T and q^{rev}