14.2: A Thermodynamics Analogy

Readers may have noticed from time to time – particularly in Chapter 9 - that I have perceived some connection between parts of classical mechanics and thermodynamics. I perceive such an analogy in developing hamiltonian dynamics. Those who are familiar with thermodynamics may also recognize the analogy. Those who are not can skip this section without seriously prejudicing their understanding of subsequent sections.

Please do not misunderstand: The hamiltonian in mechanics is not at all the same thing as enthalpy in thermodynamics, even though we use the same symbol, \( H \). Yet there are similarities in the way we can introduce these concepts.

In thermodynamics we can describe the state of the system by its internal energy, defined in such a way that when heat is supplied to a system and the system does external work, the increase in internal energy of the system is equal to the heat supplied to the system minus the work done by the system:

\[
\text{d}U = TdS - PdV. \quad \label{14.2.1}
\]

From this point of view we are describing the state of the system by specifying its internal energy as a function of the entropy and the volume:

\[
U = U(S, V) \quad \label{14.2.2}
\]

so that

\[
\text{d}U = \left( \frac{\partial U}{\partial S} \right)_V \text{d}S + \left( \frac{\partial U}{\partial V} \right)_S \text{d}V, \quad \label{14.2.3}
\]

from which we see that
\[ T = \left( \frac{\partial U}{\partial S} \right)_V \label{14.2.4} \]

and

\[ -P = \left( \frac{\partial U}{\partial V} \right)_S \label{14.2.5} \]

However, it is sometimes convenient to change the basis of the description of the state of a system from \((S, V)\) to \((S, P)\) by defining a quantity called the enthalpy \((H)\) defined by

\[ H = U + PV. \label{14.2.6} \]

In that case, if the state of the system changes, then

\[ dH = dU + PdV + VdP \label{14.2.7} \]

\[ = TdS - PdV + PdV + VdP. \label{14.2.8} \]

I.e.

\[ dH = TdS + VdP. \label{14.2.9} \]

Thus we see that, if heat is added to a system held at constant volume, the increase in the internal energy is equal to the heat added; whereas if heat is added to a system held at constant pressure, the increase in the enthalpy is equal to the heat added.

From this point of view we are describing the state of the system by specifying its enthalpy as a function of the entropy and the pressure:

\[ H = H(S, P) \label{14.2.10} \]

so that

\[ dH = \left( \frac{\partial H}{\partial S} \right)_P dS + \left( \frac{\partial H}{\partial P} \right)_S dP, \label{14.2.11} \]

from which we see that

\[ T = \left( \frac{\partial H}{\partial S} \right)_P \]

and

\[ V = \left( \frac{\partial H}{\partial P} \right)_S. \label{14.2.12} \]

None of this has anything to do with hamiltonian dynamics, so let’s move on.
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