Thermodynamics

We saw before that we can derive thermodynamics from statistical mechanics. In particular we found a microscopic interpretation of the entropy as the logarithm of $\Gamma(E,V)$, the number of available states at fixed energy, number of particles, etc. Furthermore we found a definition of temperature through the relation

$$\frac{1}{T} = \frac{\partial S}{\partial E} \qquad\qquad S = k \log \Gamma(E,V)$$

and found that the second Law of thermodynamics is statistical in nature.

We will now use these laws to derive a set of results that apply to systems in thermodynamic equilibrium. They also apply to quasistatic processes, i.e. processes which are slow enough so that the system ~~is in~~ goes through a ~~an~~ sequence of equilibrium states.

Adiabatic Processes

Consider a thermally isolated system. By this we don't mean necessarily a physically isolated system but one interacting only with external forces. The "coordinates" ~~which~~ that parametrize these forces are prescribed functions of ~~the~~ time. Hence the external forces carry no entropy of their own. An example is the slow deformation of the volume. Slow processes acting on a thermally isolated ~~s~~ system are said to be adiabatic. We will see that under such processes the entropy of the system does not change. These are reversible processes.

If a system is coupled to externally varying forces, the Hamiltonian is a function of time. Let λ be an ~~p~~ external parameter. $\Rightarrow$ the rate of change of the entropy is $\frac{dS}{dt}$. It will be a function of $\frac{d\lambda}{dt}$.

For $\frac{d\lambda}{dt}$ small enough, the leading dependence is

$$\frac{dS}{dt} \propto \left(\frac{d\lambda}{dt}\right)^2 \leftarrow \left(\text{since } \frac{dS}{dt} \geq 0\right) \Rightarrow \frac{dS}{d\lambda} \propto \frac{d\lambda}{dt}$$

$$\Rightarrow \text{ if } \cancel{\frac{dS}{dt} \Rightarrow} \ \frac{d\lambda}{dt} \to 0 \Rightarrow \frac{dS}{d\lambda} \to 0 \ (\text{reversible}).$$

⇒ Adiabatic ⇒ Reversible

but Reversible ⇏ Adiabatic

since reversible only requires $\Delta S = 0$

but in an adiabatic process the entropy of a body, which is a part of a closed system, is constant.

More precisely an adiabatic process is one in which the external conditions vary sufficiently slowly that the system is in an equilibrium state determined by the external conditions.

⇒ it has to be slow enough so that the system is able to reach equilibrium.

Let $E(p,q,\lambda)$ be the energy of the system.

$\Rightarrow$ $E = \langle E(p,q,\lambda) \rangle$ is the thermodynamic (internal) energy.

Mechanics $\Rightarrow$ $\frac{dE}{dt}(p,q,\lambda) = \frac{\partial E}{\partial t}(p,q,\lambda)$

(since $\{H,H\}_{P.B.} = 0$)

$$\Rightarrow \frac{dE}{dt}(p,q,\lambda) = \frac{\partial E}{\partial \lambda}(p,q,\lambda)\frac{d\lambda}{dt}$$

since the only explicit dependence is through $\lambda(t)$

$$\Rightarrow \frac{dE}{dt} = \left\langle \frac{dE}{dt}(p,q,\lambda) \right\rangle = \left\langle \frac{\partial E}{\partial \lambda}(p,q,\lambda) \right\rangle \frac{d\lambda}{dt}$$

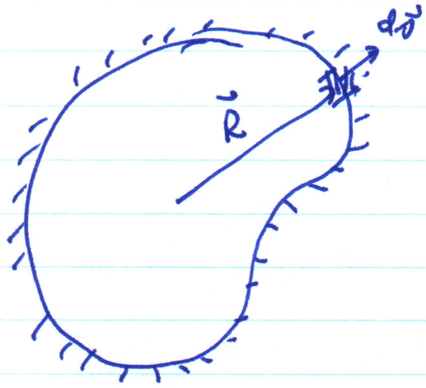
↑ fixed function of time.

Adiabatic Process $\Rightarrow$ $\left\langle \frac{\partial}{\partial \lambda} E(p,q,\lambda) \right\rangle$ is an average over the statistical distribution for an equilibrium state with fixed λ.

However, ~~for~~ since in an adiabatic process the entropy is constant $\Rightarrow$

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial \lambda}\right)_S \frac{d\lambda}{dt} \Rightarrow \boxed{\left(\frac{\partial E}{\partial \lambda}\right)_S = \left\langle \frac{\partial E}{\partial \lambda}(p,q,\lambda) \right\rangle}$$

Pressure:



In an equilibrium state, the energy and the entropy are extensive quantities (i.e. additive). In particular, the entropy is only a function of the volume for fixed E.

$\Rightarrow$ the macroscopic state of the system is determined by E, V alone.

What is the force exerted by a body on the surface that bounds it? Let $\vec{R}$ be the coordinate of a surface element.

$$\langle \vec{F} \rangle = -\left\langle \frac{\partial E}{\partial \vec{R}}(p,q,\vec{R}) \right\rangle = -\left(\frac{\partial E}{\partial \vec{R}}\right|_S$$

$$= -\left(\frac{\partial E}{\partial V}\right)_S \frac{\partial V}{\partial \vec{R}}$$

$dV = d\vec{s} \cdot d\vec{R}$

$$\Rightarrow \boxed{P = -\left(\frac{\partial E}{\partial V}\right)_S}$$ (pressure) (Pascal)

$\Rightarrow (dE)_S = -p\,dV$ in an adiabatic process.

Also $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$

$\Rightarrow T = \left(\frac{\partial E}{\partial S}\right)_V$

$\Rightarrow$ in general

$$\boxed{dE = T\,dS - p\,dV}$$

fundamental relation of thermodynamics.

Notice that $T\,dS = dQ$ (heat flow)

and $-p\,dV = dW$ (work)

$dE = \delta Q + \delta W$ (first law)

$\delta Q = T\,\delta S$ (second law for adiabatic processes)

(in general $\delta Q < T\,\delta S$)

Comments:

① dQ depends on the history of the system

② dW also depends on the history

③ dE is a function of state, independent of the history (it is an exact differential)

Specific Heats: $C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \boxed{\left(\frac{\partial E}{\partial T}\right)_V = C_V}$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

Enthalpy:

In a process at $V =$ constant $dQ = dE$

$H = E + PV$ (Legendre Transform)

$$dH = dE + PdV + VdP$$

$$= TdS - P\cancel{dV} + P\cancel{dV} + VdP$$

$$dH = TdS + VdP$$

$$\Rightarrow \left(\frac{\partial H}{\partial S}\right)_P = T$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S$$

Thermally isolated systems with $P =$ const $\Rightarrow H =$ constant

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$\Rightarrow C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\Rightarrow \boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

Free Energy (Helmholtz)

work done ~~by~~ on a body in an infinitesimal isothermal (T= const) reversible process:

$$(dW)_T = dE - dQ = dE - T\,dS = d(E-TS)$$

(T = const.)

$$F \equiv E - TS \qquad \text{free energy}$$

$$(dW)_T = dF$$

in general: $dF = dE - T\,dS - S\,dT = \cancel{T\,dS} - p\,dV - \cancel{T\,dS} - S\,dT$

$$dF = -p\,dV - S\,dT$$

$$\Rightarrow \boxed{S = -\left(\frac{\partial F}{\partial T}\right)_V} \qquad \boxed{p = -\left(\frac{\partial F}{\partial V}\right)_T}$$

$$E = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V$$

E, F, H are ~~therm~~ functions of state or thermodynamic potentials.

thermodynamic potential (Gibbs free energy) G

$$dG = -S\,dT + V\,dp \Rightarrow G = E - TS + pV = F + pV$$
$$= H - TS$$

Other parameters are also possible. Under a small change of these parameter

$$(\delta E)_{S,V} = (\delta F)_{T,V} = (\delta H)_{S,P} = (\delta G)_{T,P}$$

Away from equilibrium $\frac{dQ}{dt} < T\frac{dS}{dt}$

$$\Rightarrow \frac{dE}{dt} + p\frac{dV}{dt} = \frac{dQ}{dt} < T\frac{dS}{dt}$$

$\Rightarrow \frac{dF}{dt} < 0$ (for irreversible processes at T, V constant)

and $\frac{dG}{dt} < 0$ for irr. processes at p, T constant.

Relations between derivatives of thermodynamic functions:

(Maxwell relations)

Equation of state: a relation between T, V, P.

We will assume that the equ of state is known (later we will calculate some) and use it to relate derivatives of interesting quantities.

$$dE = TdS - p\,dV$$

⇒ since E is a function of state ⟺ ΔE is independent of the history in (S, V) ⇒

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_T} \qquad \left(\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}\right)$$

Likewise

$$dF = -SdT - p\,dV$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V}$$

These are the 4 Maxwell relations.

$$dH = TdS + Vdp$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$$

$$dG = -SdT + Vdp$$

$$\Rightarrow \boxed{-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p}$$

Also, since $S = -\left(\frac{\partial F}{\partial T}\right)_V$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = T\,\frac{\partial^2 S}{\partial V\,\partial T} = -T\,\frac{\partial^3 F}{\partial V\,\partial T^2}$$

$$= -T\,\frac{\partial^2}{\partial T^2}\left(\frac{\partial F}{\partial V}\right)_T$$

and $$\left(\frac{\partial F}{\partial V}\right)_T = -p \Rightarrow \boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V}$$

a property of the eqn of state.

Likewise $$\boxed{\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = -\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$ (2nd Maxwell Relation)

$$\boxed{\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p}$$ (4th Maxwell Relation)

From $dE = TdS - pdV$

$$\Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\Rightarrow \boxed{\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}$$

$$\Rightarrow \left(\frac{\partial E}{\partial P}\right)_T = - T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial E}{\partial T}\right)_P = C_p - P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial T}\right)_V = C_V + V\left(\frac{\partial P}{\partial T}\right)_V$$

Relation between C_p and C_V:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Jacobian: $$\frac{\partial(u\,v)}{\partial(x\,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$

$$\Rightarrow \quad \frac{\partial(v\,u)}{\partial(x\,y)} = - \frac{\partial(u\,v)}{\partial(x\,y)}$$

$$\frac{\partial(u\,y)}{\partial(x\,y)} = \left(\frac{\partial u}{\partial x}\right)_y$$

$$\frac{\partial(u\,v)}{\partial(x\,y)} = \frac{\partial(u\,v)}{\partial(w\,z)} \frac{\partial(w\,z)}{\partial(x\,y)} \qquad \text{(check!)}$$

$$\frac{\partial(u\,v)}{\partial(x\,y)} \cdot \frac{\partial(x\,y)}{\partial(u\,v)} = 1$$

$$\Rightarrow \quad C_v = T\left(\frac{\partial S}{\partial T}\right)_V = T \; \frac{\partial(S, V)}{\partial(T, V)}$$

$$= T \; \frac{\partial(S, V)}{\partial(T, p)} \Big/ \frac{\partial(T, V)}{\partial(T, p)}$$

$$= T \; \frac{\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial V}{\partial p}\right)_T - \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}$$

Since $\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p$

$$\Rightarrow \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_p + \frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)} \Rightarrow \boxed{C_V - C_p = T \; \frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)}}$$

Thermodynamic Stability

Consider a small (but macroscopic) part of a large body. We will assume that the temperature of the body is T_0 and the pressure is p_0.

$\Rightarrow$ An equivalent formulation of the 2nd law is the condition

$$G = E - T_0 S + p_0 V$$

be at a minimum in an equilibrium state.

$$\Rightarrow \delta G \geq 0$$

$$\Rightarrow \delta G = \delta E - T_0 \delta S + p_0 \delta V \geq 0$$

But

$$\delta E = \left(\frac{\partial E}{\partial S}\right)_V \delta S + \left(\frac{\partial E}{\partial V}\right)_S \delta V$$

$$+ \frac{1}{2}\left(\frac{\partial^2 E}{\partial S^2}\right)_V (\delta S)^2 + \frac{1}{2}\left(\frac{\partial^2 E}{\partial V^2}\right)_S (\delta V)^2 + \frac{\partial^2 E}{\partial S \partial V} \delta S \delta V$$

and

$$\left(\frac{\partial E}{\partial S}\right)_V = T = T_0$$

$$\left(\frac{\partial E}{\partial V}\right)_S = -P = -P_0$$

$$\Rightarrow \delta G \geq 0 \Rightarrow \cancel{\tfrac{1}{2}} \left(\frac{\partial^2 E}{\partial S^2}\right)_V (\delta S)^2 + \left(\frac{\partial^2 E}{\partial V^2}\right)_S (\delta V)^2 + 2 \frac{\partial^2 E}{\partial S \partial V} \delta S \delta V \geq 0$$

A quadratic form is positive definite iff

$\left(\frac{\partial^2 E}{\partial S^2}\right)_V > 0$ and the Hessian

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V \left(\frac{\partial^2 E}{\partial V^2}\right)_S - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 > 0$$

But $\left(\frac{\partial^2 E}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$

$$\Rightarrow \left(\frac{\partial^2 E}{\partial S^2}\right)_V > 0 \Longrightarrow \boxed{C_V > 0}$$

$$\text{Hessian} = \left(\frac{\partial^2 E}{\partial S^2}\right)_V \left(\frac{\partial^2 E}{\partial V}\right)_S - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2$$

$$= \frac{\partial\left(\left(\frac{\partial E}{\partial S}\right)_V, \left(\frac{\partial E}{\partial V}\right)_S\right)}{\partial(S, V)} = -\frac{\partial(T, P)}{\partial(S, V)} > 0$$

$$\Downarrow$$

$$\frac{\partial(T, P)}{\partial(S, V)} = \frac{\frac{\partial(T, P)}{\partial(T, V)}}{\frac{\partial(S, V)}{\partial(T, V)}} = \frac{\left(\frac{\partial P}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{T}{C_V}\left(\frac{\partial P}{\partial V}\right)_T < 0$$

$$\Rightarrow \boxed{\left(\frac{\partial P}{\partial V}\right)_T < 0}$$

$$\Longrightarrow C_p - C_V = -T \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} > 0 \Longrightarrow \boxed{C_p - C_V > 0}$$