140a Lecture 10, 2/7/19

⋆ Week 5 reading: Blundell+Blundell, chapters 14, 15, 16

• $dU = TdS - pdV$. As we discussed last time, this gives

$$T = (\frac{\partial U}{\partial S})_V, \qquad p = -(\frac{\partial U}{\partial V})_S$$

Using the fact that partial derivatives commute, this leads to

$$(\frac{\partial T}{\partial V})_S = -(\frac{\partial p}{\partial S})_V = \frac{\partial^2 U}{\partial S \partial V}$$

This is an example of a Maxwell relation. It can also be related to the statement that the Jacobian from the pV diagram to the TS diagram has unit Jacobian determinant, which is why we can compute the work from the area in either diagram

$$dTdS = \frac{\partial(T,S)}{\partial(p,V)} dpdV = dpdV, \qquad \frac{\partial(T,S)}{\partial(p,V)} = 1.$$

This is because $(\frac{\partial T}{\partial V})_S = \partial(T,S)/\partial(V,S) = \partial(p,V)/\partial(V,S) = -(\partial p/\partial S)_V$.

• $U(T,S)$ is nice if T and S are given. We can exchange conjugate variables $S \leftrightarrow T$ and $p \leftrightarrow V$ by modifying U, adding pV or subtracting TS. Consider the enthalpy $H = U + pV$ and note that $dH = dU + pdV + Vdp = TdS + Vdp$, so we get

$$T = (\frac{\partial H}{\partial S})_p, \qquad V = (\frac{\partial H}{\partial p})_S.$$

The math of going from $U(S,V)$ to $H(U,p)$ is called a Legendre transform and is similar to what you know from classical mechanics with $L(x,v)$ vs $H(x,p) = pv - L$ with $p = (\partial L/\partial v)_x$ and $v = (\partial H/\partial p)_x$.

Exercise: write down the Maxwell relation associated with $\partial^2 H/\partial S \partial p$.

• Helmholtz free energy $F = U - TS$ has $dF = -SdT - pdV$ so $F = F(T,V)$ with

$$S = -(\frac{\partial F}{\partial T})_V, \qquad p = -(\frac{\partial F}{\partial V})_T.$$

Exercise: write down the Maxwell relation associated with $\partial^2 F/\partial V \partial T$.

• Gibbs function $G = H - TS$ has $dG = -SdT + Vdp$ so $G = G(T,p)$ with

$$S = -(\frac{\partial G}{\partial T})_p, \qquad V = (\frac{\partial G}{\partial p})_T.$$

Exercise: write down the Maxwell relation associated with $\partial^2 G/\partial T \partial p$.

• Suppose that a system has initial energy U_0, and goes via some process to having energy $U(S,V)$. The system has P, T, and V, and the exterior surroundings to the system has pressure P_0 and temperature T_0. What is the work done? It depends on the process. We get

$$dU_{sys} = -\not{d}W_{mech} - P_0 dV_{sys} + \not{d}Q_{sys},$$

where we wrote the work done by the system as mechanical work (pushing a piston) plus the work done in expanding against the external pressure P_0. Moreover,

$$\not{d}Q_{sys} = -\not{d}Q_{surr} = -T_0 dS_{surr}.$$

Using $dS_{universe} = dS_{sys} + dS_{surr} \geq 0$, we get $-dS_{surr} \leq dS_{sys}$, and thus

$$\not{d}W_{mech} = -dU_{sys} - P_0 dV_{sys} + T_0 dS_{surr} \leq -d(U - T_0 S + P_0 V)_{sys}.$$

Let's write this again, in terms of the *availability*

$$A(S,V) \equiv U - T_0 S + P_0 V,$$

$$|\not{d}W|_{max} = -d(U - T_0 S + P_0 V) \equiv -dA.$$

If in equilibrium, we can use $dU = TdS - PdV$ to write

$$\not{d}W_{mech} \leq -\left((T - T_0)dS - (P - P_0)dV\right).$$

Let's interpret the two terms. The first term is the maximum work a Carnot engine would do, operating between $T_H = T$ and $T_C = T_0$: if everything were reversible, the heat leaving our system would be $Q_H = -TdS$, and that heat drives the Carnot engine, producing work $\not{d}W_{carnot} = -(T - T_0)dS$. The second term is the mechanical work, subtracting out the work done against the environment.

More generally, $\not{d}W_{mech} = PdV + \mathcal{E}dq + \vec{B} \cdot d\vec{M} + \vec{E} \cdot dP + \mu dn + \ldots \leq -dA$ applies to **all** types of work, not just PdV work.

• Example: two identical blocks, with initial temperatures $T_{1,i}$ and $T_{2,i}$. What is the maximum work that can be extracted? Solution: hook them up to a Carnot engine. Maximum work when everything is reversible. This means that the total entropy of the combined system of blocks, plus engine, should be constant. Since $\Delta S_{engine} = 0$, this means $\Delta S_{total} = \Delta S_1 + \Delta S_2$ should be zero. Implies that $T_1 T_2$ must be constant. Implies that $T_{1,f} = T_{2,f} = \sqrt{T_{1,i} T_{2,i}}$. The above formula, with S and V constant, implies $\Delta W_{max} = -\Delta U = -(\Delta U_1 + \Delta U_2) = -C(2\sqrt{T_{1,i} T_{2,i}} - T_{1,i} - T_{2,i}) > 0$.

• This illustrates a general kind of question that often comes up in thermodynamics. We start of being limited to consider equilibrium situations, because non-equilibrium processes are hard. But then broaden scope by consider bringing together two equilibrium subsystems, and study how the combined system reaches equilibrium. In general this happens such that

$$dA \leq 0, \qquad \text{with} \quad dA = 0 \quad \text{when equilibrium is restored.}$$

The above example had S constant and V constant, and so we get $dU \leq 0$, with $dU = 0$ at equilibrium. In other words, for fixed S and V, the process reaches equilibrium when U is minimized.