⋆ Week 6 reading: Blundell+Blundell, chapters 16, 18, 19

• Last time: 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

$$dU_{sys} = -\bar{d}W_{mech} - P_0 dV_{sys} + \bar{d}Q_{sys},$$

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,

$$\bar{d}Q_{sys} = -\bar{d}Q_{surr} = -T_0 dS_{surr}.$$

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

$$\bar{d}W_{mech} = -dU_{sys} - P_0 dV_{sys} + T_0 dS_{surr} \leq -d(U - T_0 S + P_0 V)_{sys}.$$

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

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

$$|\bar{d}W|_{max} = -d(U - T_0 S + P_0 V) \equiv -dA.$$

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

$$\bar{d}W_{mech} \leq -\left((T - T_0)dS - (P - P_0)dV\right).$$

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 $\bar{d}W_{carnot} = -(T - T_0)dS$. The second term is the mechanical work, subtracting out the work done against the environment.

More generally, $\bar{d}W_{mech} = PdV + \mathcal{E}dq + \vec{B} \cdot d\vec{M} + \vec{E} \cdot d\vec{P} + \mu dn + \ldots \leq -dA$ 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 $\Delta W_{max} = -\Delta U = -(\Delta U_1 + \Delta U_2) = -C(2\sqrt{T_{1,i} T_{2,1}} - T_{1,i} - T_{2,i}) > 0$.

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.

We can instead impose $U = U_1 + U_2$ fixed, with $V = V_1 + V_2$ fixed, and then equilibrium is reached when $S = S_1 + S_2$ is maximized.

• Connect to interpretation of other thermodynamic potentials, $H = U + PV$, and $F = U - ST$, and $G = U + PV - ST$. Suppose $\Delta S = 0$ and $P = P_0$, then we get $\Delta W_{mech} \leq -\Delta H$. Or if $T = T_0$ and $\Delta V = 0$, then $\Delta W_{mech} \leq -\Delta F$. Or if $T = T_0$ and $P = P_0$, then $\Delta W_{mech} \leq -\Delta G$. Now Suppose no mechanical work, $dW_{mech} = 0$. Again, $dA \leq 0$. Processes occurring in the system tend to decrease A. It reaches its minimum at equilibrium. For fixed $P_0 = P$ and $T_0 = T$, the process reaches equilibrium when G is a minimum. Likewise, for fixed T and V, the process reaches equilibrium when F is a minimum. Likewise, for fixed S and P, it reaches equilibrium when H is a minimum. For fixed S and V, the process reaches equilibrium when U is minimized. Equivalently, for fixed U and V, the process reaches equilibrium when S is maximized.

• Let's show in more detail that A decreases until it reaches its minimum, when the system is in equilibrium. Note that A is extremized if $T = T_0$ and $P = P_0$:

$$\frac{\partial A}{\partial S} = \frac{\partial A}{\partial V} = 0 \qquad \text{for} \qquad T = T_0 \quad \text{and} \quad P = P_0.$$

To show that this extremum is a minimum of A, note that, expanding near $T = T_0$ and $P = P_0$, and using $T - T_0 = (\partial A/\partial S)_V$ and $P - P_0 = -(\partial A/\partial V)_S$, we get

$$A = A_0 + \tfrac{1}{2} \left(\frac{\partial T}{\partial S}\right)_V (\Delta S)^2 + \left(\frac{\partial T}{\partial V}\right)_S \Delta S \Delta V - \tfrac{1}{2} \left(\frac{\partial P}{\partial V}\right)_S (\Delta V)^2 + \dots.$$

We see that $A > A_0$ provided that

$$\left(\frac{\partial T}{\partial S}\right)_V > 0 \qquad \text{which is equivalent to} \qquad C_V > 0,$$

$$\left(\frac{\partial P}{\partial V}\right)_S < 0 \qquad \text{which is equivalent to} \qquad \kappa_S \equiv -\left(\frac{\partial \ln V}{\partial p}\right)_S > 0,$$

$$\text{and} \qquad \left(\frac{\partial T}{\partial V}\right)_S^2 < -\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_S.$$

Here κ_S is the coefficient of adiabatic compressibility.

• Third "law" of thermodynamics. Recall $S(T) = S(T_0) + \int_{T_0}^T C dT/T$. The statement is that it is almost always the case that $S(T \to 0) \to 0$ (Planck) or $S'(T \to 0) \to 0$ (Nernst). In theories with non-degenerate groundstates (which is almost always the case), $\Omega(E \to 0) \to 1$, and then $S = k_B \ln \Omega \to 0$. Counterexamples to the 3rd law arise if $S(T \to 0) = S_0 \neq 0$, which can happen if the groundstate is degenerate. **Today!: special colloquium at 4pm by Prof. Sachdev (Harvard) on Strange Metals and Black Holes, might mention some examples where $S(0) \neq 0$, e.g. charged black holes.** A consequence of assuming $S(0) = 0$ is that $C(T \to 0) \to 0$; if $C(0) \neq 0$, there would be a problem as $T \to 0$ in $\int dT/T = \ln T \to -\infty$. Also $(\partial S/\partial p)_T \to 0$ which, by a Maxwell relation, implies $(\partial \ln V/\partial T)_p \to 0$. The third "law" implies that gasses cannot be ideal at $T \to 0$. Draw two curves in a (T, S) diagram, with $S(T \to 0) \to 0$ for both, and picture the infinite number of steps needed to cool to $T \to 0$.

• Equipartition of energy. Recall the viral theorem from classical mechanics: if $V(\alpha \vec{r}_i) = \alpha^k V(\vec{r}_i)$, then $2\langle KE \rangle = k\langle V \rangle$ where here the average is over a cycle. For a SHO, $k = 2$ and this gives $\langle KE \rangle = \langle V \rangle$. Indeed, from $x = A\cos(\omega t + \phi)$ we see $\langle KE \rangle = \langle V \rangle = \frac{1}{2}E$. The SHO is ubiquitous in Nature because any restoring potential can be Taylor expanded for small oscillations around equilibrium and then looks approximately like a SHO. We saw with the Maxwell velocity distribution that, in thermal equilibrium at temperature T, $\langle \frac{1}{2}m\vec{v}^2 \rangle = \frac{3}{2}k_B T$. Similarly, for a SHO we can have $P(x) = Ce^{-\beta \alpha x^2}$ which gives $\langle \alpha x^2 \rangle = \frac{1}{2}k_B T$ (note it is independent of the spring constant α, just as the average KE is independent of m). Similar consideration applies to rotational degrees of freedom. The upshot is $\langle E \rangle = \frac{f}{2}k_B T$ where f is every degree of freedom: 3 for translations, plus any applicable vibrations, rotations. This is called the equipartition theorem. As we already discussed, for an ideal gas this gives $U = \frac{f}{2}Nk_B T$ so $C_V = \frac{f}{2}Nk_B$ and $C_P = (\frac{f}{2}+1)Nk_B T$ so $\gamma = 1 + (2/f)$. The equipartition theorem necessarily breaks down, e.g. applying it naively leads to the UV catastrophe in the blackbody spectrum, which led to Planck's introduction of his constant to fix the problem, giving the birth of QM. We will discuss this more later.