140a Lecture 8, 1/31/19

⋆ Week 4 reading: Blundell+Blundell, chapters 13, 14

• Emphasize how powerful a statement it is that something is a state variable. E.g. $dU = đQ + đW = đQ_R + đW_R$, with $đW_R = -pdV$. Can compute $\Delta U = \int_i^f dU$ by considering any path between the initial and final states, even for irreversible processes, e.g. free expansion of an ideal gas. Also, can compute ΔV for any process, even irreversible, via $\Delta V = -\int_i^f đW_R/p$ for a reversible path with the same endpoints. Emphasizing this because similar statements will apply to $\Delta S = \int đQ_R/T$.

• Last time: consider an arbitrary system $\mathcal{O}$ undergoing an arbitrary cyclic process. Divide into N infinitesimal steps during which the temperature is constant, $T_1 \ldots T_N$ and let Q_i be the heat absorbed by the system while at temperature T_i. Now couple each step to a tiny Carnot engines / refrigerators C_i, whose heat output is chosen to be $\mathcal{O}$'s input on the i-th step. The Carnot engines output is heat Q_i and temperature T_i and their input is heat $Q_i^* = T_* Q_i / T_i$ at temperature $T_* > T_i$. The Carnot engines have input $W_i = Q_i - Q_i^*$. The system $\mathcal{O}$ does work $W_{\mathcal{O}} = \sum_i Q_i$ and the total work done by combining the system and the attached Carnot engines is $W_{total} = W_{\mathcal{O}} - \sum_i W_i = \sum_i Q_i^*$, which is the total heat taken from a reservoir at T^*. Kelvin's statement implies that $W_{total} < 0$:

$$\sum_i Q_i^* \le 0, \qquad \text{i.e.} \qquad \sum_i \frac{Q_i}{T_i} \le 0, \qquad \text{i.e.} \qquad \oint \frac{đQ}{T} \le 0.$$

(Actually, we can replace $T \to T_{ext}$ here, allowing for the fact that the temperature T of the system need not be be in equilibrium with the external surroundings.) For a reversible cycle we can reverse to get inequality with $đQ \to -đQ$ (and $T_{ext} = T$), so

$$\oint \frac{đQ_R}{T} = 0.$$

Note difference between $đQ/T_{ext}$ and $đQ_R/T$.

• So $đQ_R/T = dS$ is a state variable! Like $-đW_R/p = dV$ is a state variable.

• So $S(B) - S(A) = \int_A^B đQ_R/T$ over any reversible path.

• Thus $\int_A^B đQ/T \le S(B) - S(A)$, with equality iff reversible.

• Entropy of thermally isolated ($đQ = 0$) system never decreases: $S_f - S_i \ge 0$. Comment on the arrow of time. Thermally isolated system is in state of maximum entropy, consistent with external constraints. If not thermally isolated, $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \ge 0$, with equality iff the process is reversible.

• E.g. heat $|Q|$ going from T_2 to T_1 has $\Delta S = |Q|(T_1^{-1} - T_2^{-1})$ is properly positive iff $T_2 > T_1$, recovering Clausius's statement.

E.g. heat engine: $\Delta S_{total} = \Delta S_{engine} + \Delta S_H + \Delta S_C \geq 0$, with $\Delta S_{engine} = 0$ since it is cyclic, and $\Delta S_H = -|Q_2|/T_2$ and $\Delta S_C = |Q_1|/T_1$. Gives $|W| \leq |Q_2|(1 - T_1/T_2)$, with equality iff the process is reversible. Carnot's statement.

• E.g. put C_1 and C_2 objects at T_1 and T_2 into thermal contact. Work out T_f and ΔS. Consider limit $C_1 \to \infty$. Show that $\Delta S \geq 0$ and equal zero iff $T_1 = T_2$.

• For an ideal gas, $dU = C_V dT$ and $pdV = Nk_B T dV/V$ so

$$S_f - S_i = \int_i^f (dU + pdV)/T = C_V \ln(\frac{T_f}{T_i}) + Nk_B \ln(\frac{V_f}{V_i}) = C_P \ln(\frac{T_f}{T_i}) - Nk_B \ln(\frac{p_f}{p_i}).$$

Recall $C_P = C_V + Nk_B$ for an ideal gas.

• E.g. gas in a container of volume V_1 suddenly expands to volume V_2. Irreversible. Compute ΔS from any reversible path, e.g. a reversible isotherm, to get $\Delta S = Nk_B \ln(V_2/V_1)$. In the reversible version, this is balanced out by the entropy change of the heat reservoir. In the irreversible process, there is no heat reservoir and process causes $\Delta S_{universe} > 0$.

• E.g. two different ideal gasses in two containers, and then the partition is removed, get

$$\Delta S_{mixing} = N_1 k_B \ln(\frac{V_1 + V_2}{V_1}) + N_2 k_B \ln(\frac{V_1 + V_2}{V_2})$$

(discuss the Gibbs paradox, will return to it later). If $T_1 \neq T_2$, also get

$$\Delta S_{T_i \to T_f} = C_{V,1} \ln(\frac{T_f}{T_1}) + C_{V_2} \ln(\frac{T_f}{T_2}).$$

Can verify that each of these contributions are positive, e.g. if $C_{V,1} = C_{V,2} = C$ then $T_f = \frac{1}{2}(T_1 + T_2)$.