140a Lecture 9, 2/5/19 HAPPY CHINESE NEW YEAR!!!

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

• Consider heat Q that flows out of bath at T_2, then irreversibly down to T_1, and then via a reversible engine down to T_0. If the reversible step were omitted, $W_{max} = Q(1-\frac{T_0}{T_2})$. Because of the reversible step, now $W'_{max} = Q(1-\frac{T_0}{T_1})$. So the wasted energy is $W_{max} - W'_{max} = Q(\frac{T_0}{T_1} - \frac{T_0}{T_2}) = T_0\Delta S$, which illustrates that irreversible processes, producing entropy, wastes available energy ...*forever*. Illustrates how ΔS_{total} is a measure of the degradation of energy. Quality vs quantity: energy is the quantity, conserved regardless, irrespective of whether or not it is useful. But ΔS accounts for the inevitable, and irreversible, degradation of energy, towards a useless quality form.

We will soon consider the Helmholtz free energy $F = U - TS$, we will see that F measures the maximum work that a system can do with fixed temperature and volume $W \leq -\Delta F$.

• Slope of isochoric and isobaric curves in a TS diagram:

If $dV = 0$ then $dU = C_V dT = TdS$, so slope $dT/dS = T/C_V$. If $dp = 0$ then $dU + pdV = d(U + pV) = C_p dT = TdS$, so slope $dT/dS = T/C_p$.

Recall for an ideal gas:

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

Can verify the above dT/dS using these.

• $dU = đQ + đW = đQ_R + đW_R = TdS - pdV$. This means that $U = U(S, V)$ and

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

$$\to \frac{p}{T} = -(\frac{\partial U}{\partial V})_S(\frac{\partial S}{\partial U})_V = (\frac{\partial S}{\partial V})_U.$$

The last identity follows from combining $dU = (\frac{\partial U}{\partial S})_V dS + (\frac{\partial U}{\partial V})_S dV$ and a similar formula for $dS(V, U)$.

Check and verify it for an ideal gas.

• Recall our earlier discussion that the system is in equilibrium when it has the largest possible Ω and how this for combining systems reproduces the condition that equilibrium is when the temperatures are equal, with $\frac{1}{k_B T} = \frac{d \ln \Omega}{dE}$. Comparing with $T = (\frac{\partial U}{\partial S})_V$, this gives the Boltzmann formula

$$S = k_B \ln \Omega.$$

More on arrow of time and increasing randomness.

• Gibbs' expression: $S = -k_B \sum_i P_i \ln P_i$. Divide the N microstates into groups of macrostates, with n_i microstates in the i-th macrostate, so $N = \sum_i n_i$. The probability of finding the i-th macrostate is $P_i = n_i/N$ assuming that all are equally likely. Then $S_{tot} = k_B \ln N = S + S_{micro}$, where $S_{micro} = \sum_i P_i S_i$ and $S_i = k_B \ln n_i$ is the entropy of the microstates in each macrostate. The observed entropy is $S = S_{tot} - S_{micro} = k_B \sum_i P_i \ln P_i$. In the HW you will use $P_i = e^{-\beta E_i}/Z$ to obtain $S = k_B \ln Z + \beta U$, where $\beta = 1/k_B T$.

• Shannon Information theory: $Q = -k \ln P$ is a measure of the information content (surprise) of a statement, where P is the probability that it is true. If $P = 1$, then there is no surprise, while if $P \ll 1$ then we are very surprised if it occurs. The Shannon entropy $S = \langle Q \rangle = \sum Q_i P_i$ is the expected surprise. In quantum mechanics, we can replace a pure state with a mixed state density matrix $\rho = \sum_i P_i |\psi_i\rangle\langle\psi_i|$ to account for classical probability of different states. Then $S(\rho) = -\mathrm{Tr}(\rho \ln \rho)$. In thermal physics we take $\rho = \exp(-\beta H)$. There is a nice discussion in chapter 15, which we will mostly skip because of time and topic constraints; perhaps it will be discussed more in 140b.

• Discuss Maxwell's demon and the entropy vs information in its mischievous brain.