

140a Lecture 2, 1/10/19

★ Week 1 reading: Blundell+Blundell, chapters 1,2,3,4.

- Last time: some thermodynamic variables: pressure p , volume V , temperature T . The 0-th law of thermodynamics is that one can define temperature as a property of a system. Equilibrium requires $\phi_A(P_A, V_A) = \phi_B(P_B, V_B) = \phi_C(P_C, V_C)$ and we can define $\phi(p, V)$ to be the temperature. Generally, equilibrium occurs on a 2d surface in the 3d space of (P, V, T) . Bring in model for water's interesting equilibrium phase surface. Example: the ideal gas law, $PV = nRT = nk_B T$, in the dilute limit (as in the model).

- Units: recall that pV has units of energy. We will see that $\delta W_{reversible} = -pdV$, consistent with the units. Also heat δQ has units of energy.

- Temperature T will always in this class be described in units of Kelvin, which is such that $T \geq 0$ (we will mention some bizarre contrary cases). In these units, $k_B T$ has units of energy. E.g. room temperature is $T_{room} \approx 300K$ and $k_B T_{room} \approx (1/40)eV \approx 4 \times 10^{-21} J$. k_B is not a fundamental constant, but is just a conversion factor because we choose to measure temperature with a particular set of units, rather than directly in the same units as energy. The reason that $k_B T$ is so small is because that is \sim the kinetic energy of a single molecule in thermal equilibrium. So to get to macroscopic energies from everyday life we have to multiply it by something like $N_A \approx 6.02 \times 10^{23}$. In chem class, usually write $n = N/N_A$ as number of mols and $R = k_B N_A$, so $nR = Nk_B$; we'll use N and k_B .

- Extensive vs intensive variables: a variable is extensive if its value for a whole system is the sum of the values for subsystems; an intensive variable is the same for the subsystems and the whole system. So extensive variables include volume V , mass M , number of molecules N . Intensive variables include pressure p , and temperature T .

- A thermodynamic system can be described by the state variables (p, V, T) . They just depend on the state of the system, not the history of how it got to that state. A thermodynamic system is in thermodynamic equilibrium if these variables are on a surface where some $f(p, V, T) = 0$. For example, for an ideal gas, it is $f = pV - Nk_B T = 0$. Note that the two terms in f here have the same units (energy) and are extensive; whenever you write something, you should check that the units make sense and that the extensive vs intensive property makes sense (e.g. that all terms added together have the same scaling with the size of the system). Look at the model of (p, V, T) for examples, e.g. water, and note that different systems differ in many regions, and have interesting phases (liquid, solid, etc) – it is only in the dilute limit that all behave approximately like an ideal gas.

- Consider N particles which can each have two energy states, say $E = 0$ and $E = \epsilon$. Q: How many configurations Ω of the whole system have $E = r\epsilon$? A: $\Omega(E = r\epsilon) = \binom{N}{r} = N!/r!(N-r)!$. Remember, Ω is a number (so it is dimensionless).

- If a subsystem has energy E_1 and number of states $\Omega_1(E_1)$ and another subsystem has energy E_2 and number of states $\Omega_2(E_2)$, the whole system, including both, has energy $E = E_1 + E_2$ (energy is extensive) and $\Omega(E) \approx \Omega_1(E_1)\Omega_2(E_2)$ (the error becomes negligible for large subsystems when the interactions are negligible, or the relation is exact for decoupled subsystems). So $\ln \Omega$ is extensive. Boltzmann: $S = k_B \ln \Omega$ is the stat mech description of entropy; we will discuss this much more throughout the class – just mentioning it now as a preview.

- Statistical definition of temperature: the two subsystems are in equilibrium if Ω is maximized. Reason: assume that all microstates are equally likely, so the most likely configuration once equilibrium is achieved is that with the most possible states. Transfer energy between subsystems 1 and 2 until $\Omega_1(E_1)\Omega_2(E_2)$ is maximized, with $dE_1 = -dE_2$ since energy is conserved. Write $\frac{d}{dE_1} \ln(\Omega_1(E_1)\Omega_2(E - E_1)) = 0$ to maximize, so $d \ln \Omega_1 / dE_1 = d \ln \Omega_2 / dE_2$ for equilibrium. Note that $d \ln \Omega / dE$ is intensive (since it is the ratio of two extensive variables) and has units of 1/energy. In fact,

$$\frac{d \ln \Omega(E)}{dE} = \frac{1}{k_B T} \equiv \beta \quad \text{a key equation!}$$

Micro-canonical ensemble: a collection of copies of the system all with the same energy, and then we obtain temperature as above.

- Canonical ensemble: put a small system in thermal contact with a large heat bath, at temperature T . Energy can be exchanged with the heat bath, so the small system does not have a fixed ϵ but instead has a probability distribution $P(\epsilon) \propto \Omega(E - \epsilon) \times 1$, associated with the number of states of the heat bath (the $\times 1$ is because the system itself is small, without inner possibilities, so we assume for the moment that it has non-degenerate states – this can, and should, be modified as appropriate). By a Taylor series in small ϵ find $\Omega(E - \epsilon) \approx \Omega(E)e^{-\beta\epsilon}$, so

$$P(\epsilon) = Z^{-1}e^{-\beta\epsilon}, \quad \text{where} \quad Z(\beta) \equiv \sum_{\epsilon} e^{-\beta\epsilon}.$$

$Z(\beta)$ is the partition function, a key quantity in statistical mechanics.