

★ Week 2 reading: Blundell+Blundell, chapters 5,6. Then skip to chapter 11.

• Last time: Canonical $P(E) \propto e^{-E/k_B T}$ for the case of the MB distribution gives $P(\vec{v}) = e^{-m\vec{v}^2/2k_B T}$ gives $\langle \vec{v}^2 \rangle = 3k_B T/m$ and $pV = Nk_B T$. For an ideal monatomic gas, we get $pV = \frac{2}{3}U$ where U is the total internal energy, which is also nice to write (as we will discuss today) as $U = C_V T$ with $C_V = \frac{3}{2}Nk_B$.

• **Highly recommended for this class: Feynman lectures on physics, volume 1, chapters 38-46.** They are free online, and I added a link on the webpage.

• Gas law for photons (see Feynman lecture 39). We saw last time that $p = \frac{N}{V} \langle p_z v_z \rangle$ (recall the 2s) for a wall (or a pretend wall) with normal in the z direction. Since p is a rotational scalar, this is better written as $p = \frac{N}{V} \frac{1}{3} \langle \vec{v} \cdot \vec{p} \rangle$. This formula works even for light (a gas of photons) in thermal equilibrium (blackbody spectrum), even though photons are massless (recall their $\vec{p} = \hbar \vec{k}$ and $E = \hbar \omega$). Recall from relativity that $\vec{v} = c^2 \vec{p} / E$, so $\vec{v} \cdot \vec{p} = c^2 p^2 / E$ and for photons $E = cp$ so $\vec{v} \cdot \vec{p} = E$ so we find that photons have $pV = U/3$ for photons. Later (B^2 chapter 23), we will see that photons have $U = V(4\sigma_{SB}/c)T^4$ where σ_{SB} is the Stefan-Boltzmann constant, which we will derive from statistical mechanics and quantum mechanics ($\sigma_{SB} = \pi^2 k_B^4 / 60c^2 \hbar^3$).

• Exponential atmosphere example: a molecule of mass m in the atmosphere has potential energy mgh , where h is the height. The general expression $P(E) \propto e^{-E/k_B T}$ then leads to an extra factor of $e^{-mgh/k_B T}$ in the probability distribution. This implies that the number density $n = N/V$ for fixed T varies with h as $n = n_0 e^{-mgh/k_B T}$. This can also be derived by balancing the forces on a slice of air between h and $h + dh$, where the pressure differential between the top and bottom balances the weight of the air in the slice, so $dp = dnk_B T = -mgndh$.

• Chapter 11. The first law of thermodynamics. Demo of heat engine, and how thermodynamics grew from desire to convert some heat ΔQ into work ΔW , and observed impossibility of perpetual motion machines. This led to the concept of conservation of energy. We will discuss it, and will write it as $dU = \not{d}Q + \not{d}W$, with $\not{d}W_{rev} = -pdV$. Explain the \not{d} and the minus sign.

• Let's start with the math of what \not{d} denotes. This notation is not common outside of thermodynamics, but could be used more generally. It comes from the fact that we want to call some small change of something (e.g. work) as $d(\text{something})$, but d means two different things: small, and an exact differential, and not everything is both. The \not{d} means small change but not an exact differential, whereas d means an exact differential.

Consider a function $F(x, y)$, and then note that $dF = \partial_x F dx + \partial_y F dy$; this is an example of what is called an exact differential. Note that $\int_{\Gamma} dF = F(x_b) - F(x_a)$ depends only on the endpoints, not on the path Γ , and correspondingly $\oint_{\Gamma} dF = 0$ for any closed Γ . On the other hand, consider some $\not dG \equiv G_x(x, y)dx + G_y(x, y)dy$ and note that generally $\int_{\Gamma} \not dG$ depends on the path Γ , and generally $\oint_{\Gamma} \not dG \neq 0$ for closed paths. By Stokes theorem, this is because generally the curl $\partial_y G_x - \partial_x G_y \neq 0$. The condition for these integrals to be path independent, and to vanish for any closed path, is that the curl should be zero, $\partial_y G_x - \partial_x G_y = 0$. Then locally (modulo what is called non-trivial cohomology but we won't discuss that more here), $G_x = \partial_x F$ and $G_y = \partial_y F$, i.e. the vector field with zero curl can locally be written as a gradient. (For those of you who took my 105a class last year, recall analytic functions and the Cauchy-Riemann equations.) The $\not d$ is a reminder that the quantity is not an exact differential, so it can have non-zero curl. Example: $\not dG \equiv ydx$ has $\oint \not dG = A_{enclosed}$. On the other hand, $dG = ydx + xdy = d(xy)$ has $\oint dG = 0$.

An example from outside thermodynamics: the EMF change (work against electric force per unit charge) $\not d\mathcal{E} = \vec{E} \cdot d\vec{\ell}$ can have non-zero EMF around a closed loop if there is a time-dependent magnetic flux through the loop, and that is how we can make motors or electrical generators via wire coils and magnets. We usually just write it in terms of $\vec{E} \cdot d\vec{\ell}$ and use the statement that \vec{E} can have non-zero curl, instead of defining $\not d\mathcal{E}$. The issue in thermodynamics is that the two main quantities, heat and work elements, are useful notions. We could just write $-pdV$ instead of work and TdS instead of heat, but that would obscure things. As we will now discuss, it is a good thing that $\not dW$ and $\not dQ$ are not exact differentials – that is how cyclic engines can convert heat into work!

- PV diagrams for pistons. Consider gas in a piston, with pressure p and suppose that the piston is allowed to expand *reversibly*. What this means is that the expansion is close to equilibrium, so the forces are approximately balanced between the internal pressure and the mechanical device that the piston is pushing against. The work done **by** the gas on the piston if its pressure is p and its change of volume is $dV = Adx$ is pdV , and the work done **on** the gas inside by the piston is $-pdV$. Following the textbook, we will define $\not dW = -pdV$ to be the work done **on** the system (some books instead define it to be the work by the system and then $\not dW_{there} = -\not dW_{here}$). Example of a closed rectangle in the pV plane, with $\oint \not dW = \pm A_{enclosed}$, and the convention for the path orientation and overall sign.

- Conservation of energy $dU = \delta Q + \delta W$. Sometimes I call $U = E$. U is the total internal energy, and it is a state variable. For an ideal gas, $U = U(T)$.

- Discuss heat, and heat capacity. $C_V \equiv (\frac{\partial Q}{\partial T})_V$ and $C_P \equiv (\frac{\partial Q}{\partial T})_P$. Note that both are extensive, and it is convenient to define the specific heats $c_V = C_V/M$ and $c_P = C_P/M$, which just depend on the material (and in general T), independent of the size of the sample.