140a Lecture 3, 1/15/19

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

• Let's recap some highlights from last lecture. We considered two closed subsystems in thermal contact. The macroscopic condition for them to be in thermal equilibrium is some $\phi_A(p_A, V_A) = \phi_B(p_B, V_B)$, and we can call that quantity temperature, $T_A = T_B$, with $k_B T$ an energy. The microscopic condition for thermal equilibrium is that the total number of configurations $\Omega_A(E_A)\Omega_B(E - E_A)$ is a maximum as a function of E_A, which implies that $\frac{d}{dE_A} \ln \Omega_A(E_A) = \frac{d}{dE_B} \ln \Omega_B(E_B)$ and this should be the same as their temperatures being equal. So, in the microcanonical ensemble description we consider a system (an ensemble of systems) of fixed E, and then determine T via

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

In the canonical ensemble description, we have systems in thermal contact with a heat bath, so temperature T is that of the bath and a 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

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

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

• Maxwell-Boltzmann distribution. For a dilute gas, we can ignore interactions and each molecule has $\epsilon = \frac{1}{2}m\vec{v}^2$ if it's monatomic (additional, rotational energy if it's not monatomic, will mention more about that shortly). How dilute is typical? $N/V \sim 6 \times 10^{26}/22m^3 \sim 3 \times 10^{25}m^{-3}$, so $(V/N)^{1/3} \sim 10^{-8}m$ which is much larger than the size of a molecule. The MB distribution is $P(\vec{v})d^3\vec{v}$ with $P(\vec{v}) \propto e^{-\beta\frac{1}{2}m\vec{v}^2}$. The $P(\vec{v})$ is of the form above for $P(\epsilon)$, with $\epsilon = \frac{1}{2}m\vec{v}^2$ the kinetic energy. The $d^3\vec{v}$ can be understood as coming from $d^3\vec{r}d^3\vec{p}$ phase space volume. A motivation for this is Liouville's theorem: by Hamilton's equations, classical systems move through phase space like an incompressible fluid. In QM, the uncertainty principle makes phase space into discrete pixels, so can get sums over phase space instead of integrals, which is kind of nice.

Note that $P(\vec{v}) = p(v_x)p(v_y)p(v_z)$, where each is a Gaussian normal distribution. The fact that it's a product makes sense: the three components are decoupled, so the probability

for some $\vec{p}$ should be the product of that for the separate components – probabilities of decoupled **and** statements multiply. Also, the fact that it depends only on the scalar $\vec{v}^2$ makes sense, by rotational invariance; these two requirements are pretty much sufficient to determine the Gaussian form. If we just consider $p(v_x)$, find $\langle v_x \rangle = 0$ and $\langle v_x^2 \rangle = k_B T/m$, so increasing temperature increases the standard deviation. For the speed distribution, integrate $d^3\vec{v}$ in spherical coordinates to get $4\pi v^2 dv$ and then $P(v)dv = Cv^2 e^{-mv^2/2k_B T}$, where $C = (4/\sqrt{\pi})(m/2k_B T)^{3/2}$. Find $\langle v^2 \rangle = 3k_B T/m$, so $v_{RMS} \approx \sqrt{3k_B T/m}$. For air we get $m \approx 30 m_{proton} \approx 30 GeV/c^2 \approx 30 \times 10^{-3} kg/6.02 \times 10^{23}$. Get $v_{RMS} \approx 500 m/s$.

Note that $\langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}k_B T$. This is an example of the classical equipartition theorem, that each d.o.f. has average energy $\frac{1}{2}k_B T$. The average total internal energy of a gas of N non-interacting, monatomic atoms, in thermal contact with a heat bath at temperature T, is then $U = \frac{3}{2}Nk_B T$. For diatomic or polyatomic molecules, again approximately non-interacting, we have instead $U = \frac{f}{2}Nk_B T$, where f is the number of translation or rotational degrees of freedom of each molecule. It is interesting that dU/dT is a macroscopic observable, which can be measured for different gasses, and which reveals the value of f which has something to do with the individual molecules.

• Pressure with MB velocity distribution: suppose a wall is at $z = 0$, with $z > 0$ inside the container. The particles with $v_z < 0$ will hit the wall. The number of particles hitting the wall area A in time dt is $(N/V)A|v_z|dt$. Each such particle reflects off the wall, imparting impulse $2m|v_z|$. The pressure on the wall is thus

$$ p = \frac{N}{V}2m \int_{v_z > 0} d^3\vec{v} P(\vec{v})v_z^2 = \frac{N}{V}m\langle v_z^2 \rangle = \frac{N}{3V}m\langle \vec{v}^2 \rangle = \frac{N}{V}k_B T. $$

This gives the ideal gas law, $pV = Nk_B T$. Show how the $1/3$ factor also comes from averaging $\cos^2 \theta$ in spherical coordinates.

• For fun: estimate the number $N/V = p_{atm}/k_B T$ of air molecules in a cubic meter of volume at STP, and their mass. Recall $p_{atm} \approx 10^5 Pa$.