Pre-class Preparation

**Wednesday**
Read: Chapter 6, Sec. (6.4) (What is thermodynamics?) and (6.5) (Mechanics: friction and fluctuations)

1. **Langevin dynamics.** (Computational) ②

   Even though energy is conserved, macroscopic objects like pendulums and rubber balls tend to minimize their potential and kinetic energies unless they are externally forced. Section (6.5) explains that these energies get transferred into heat – they get lost into the $6N$ internal degrees of freedom. Equation (6.49) suggests that these microscopic degrees of freedom can produce both friction $\gamma$ and noise $\xi(t)$.

   (a) First consider the equation $\ddot{h} = \xi(t)$. Assume $\xi(t)$ gives a ‘kick’ to the particle at regular intervals separated by $\Delta t$: $\xi(t) = \sum_{j=-\infty}^{\infty} \xi_j \delta(t - j\Delta t)$, with $\langle \xi_j^2 \rangle = \sigma^2$ and $\langle \xi_i \xi_j \rangle = 0$ for $i \neq j$. Argue that this leads to a random walk in momentum space. Will this alone lead to a thermal equilibrium state?

   (b) Now include the effects of damping, which reduces the momentum by $\exp(-\gamma \Delta t)$ during each time step, so $p_j = \exp(-\gamma \Delta t)p_{j-1} + m\xi_j$. By summing the geometrical series, find $\langle p_j^2 \rangle$ in terms of the mass $m$, the noise $\sigma$, the damping $\gamma$, and the time step $\Delta t$.

   (c) What is the relation between the noise and the damping needed to make $\langle p^2 / 2m \rangle = \frac{1}{2} k_B T$, as needed for thermal equilibrium?

   This is *Langevin dynamics*, which both is a way of modeling the effects of the environment on macroscopic systems and a numerical method for simulating systems at fixed temperature (*i.e.*, in the canonical ensemble).

**Friday**
Read: Chapter 6, Sec. (6.6) (Chemical equilibrium) and (6.7) (Free energy density)
2. Newton’s theory of sound. ②

Note that our derivation of the diffusion equation (6.67) for perfume in still air ignored the air molecule degrees of freedom. Without saying so, we have integrated out the air degrees of freedom – allowing the perfume molecules to exchange momentum and energy locally with a ‘bath’ of air molecules. Let us consider the effective equation of motion for an ideal gas with a locally conserved momentum, but at constant temperature (exchanging heat but not momentum with its environment.)

If the mass of the ideal gas atoms is \( m \), the momentum density is \( \Pi(x) = m J(x) \), where \( J(x) = \rho(x) v(x) \) is the particle current and \( v(x) \) is the mean particle current. Newton’s law \( F = \dot{p} = ma \) turned into densities tells us that \( \dot{\Pi} = F(x) \), where the force density \( F(x) = -\rho(x) \partial \mu / \partial x \), the density of particles times the force per particle.

Using \( \partial \rho / \partial t = -\partial J / \partial x \), find \( \partial^2 \rho / \partial t^2 \) in terms of \( \rho \) and \( \partial \mu / \partial x \). Use the ideal gas law eqn (6.65) for \( \mu(x) \) to find \( \partial^2 \rho / \partial t^2 \). What law emerges? What is the speed of sound?

(\text{Newton originally proposed this calculation in the} \textit{Principia}; it was later pointed out by Laplace that sound vibrations are too fast to exchange heat with their surroundings.)

Exercises

6.3abcd: Negative temperature, parts (a-d) only. (Note that you’ve done this calculation already in disguise: see the rubber band.)

6.11: Barrier crossing

A.13: Nucleosynthesis as a chemical reaction. (Look up the entropy of a thermal gas of photons.)

1. Nucleosynthesis as a chemical reaction① (Astrophysics) ③

The very early Universe was so hot that any heavier nuclei quickly evaporated into protons and neutrons. Between a few seconds and a couple of minutes after the Big Bang, protons and neutrons began to fuse into light nuclei – mostly helium. The energy barriers for conversion to heavier elements were too slow, however, by the time they became entropically favorable. Almost all of the heavier elements on Earth were formed later, inside stars.

In this exercise, we explore a hypothetical universe with faster nucleosynthesis reactions, or slower expansion, so that the reactions remained in equilibrium. Clearly the nucleons for the equilibrated Universe will all fuse into their most stable form.\(^2\) The binding energy \( \Delta E \) released by fusing nucleons into \( ^{56}\text{Fe} \) is about \( 5 \times 10^8 \text{ eV} \) (about half a proton

\(^1\)This exercise was developed in collaboration with Katherine Quinn.

\(^2\)It is usually said that \( ^{56}\text{Fe} \) is the most stable nucleus, but actually \( ^{62}\text{Ni} \) has a higher nuclear binding energy per nucleon. Iron-56 is favored by nucleosynthesis pathways and conditions inside stars, and we shall go with tradition and use it for our calculation.
mass). In this exercise, we shall ignore the difference between protons and neutrons,\(^3\) ignore nuclear excitations (assuming no internal entropy for the nuclei, so \(\Delta E\) is the free energy difference), and ignore the electrons (so protons are the same as hydrogen atoms, etc.)

The creation of \(^{56}\text{Fe}\) from nucleons involves a complex cascade of reactions. We argued in Section (6.6) that however complicated the reactions, they must in net be described by the overall reaction, here

\[
56p \rightarrow ^{56}\text{Fe},
\]

releasing an energy of about \(\Delta E = 5 \times 10^8\) eV or about \(\Delta E/56 = 1.4 \times 10^{-12}\) joules/baryon.

We used the fact that most chemical species are dilute (and hence can be described by an ideal gas) to derive the corresponding law of mass–action, here

\[
[\text{Fe}]/[p]^{56} = K_{eq}(T).
\]

(Note that this equality, true in equilibrium no matter how messy the necessary reactions pathways, can be rationalized using the oversimplified picture that 56 protons must simultaneously collect in a small region to form an iron nucleus.) We then used the Helmholtz free energy for an ideal gas to calculate the reaction constant explicitly \(K_{eq}(T)\) for a similar reaction, in the ideal gas limit.

(a) Give symbolic formulas for \(K_{eq}(T)\) in eqn (2), assuming the nucleons form an approximate ideal gas. Reduce it to expressions in terms of \(\Delta E\), \(k_B T\), \(h\), \(m_p\), and the atomic number \(A = 56\). (For convenience, assume \(m_{Fe} = A m_p\), ignoring the half-proton-mass energy release. Check the sign of \(\Delta E\): should it be positive or negative for this reaction?) Evaluate \(K_{eq}(T)\) in MKS units, as a function of \(T\). (Note: Do not be alarmed by the large numbers.)

Wikipedia tells us that nucleosynthesis happened “A few minutes into the expansion, when the temperature was about a billion . . . Kelvin and the density was about that of air”. To figure out when half of the protons would have fused ([Fe] = [p]/A), we need to know the temperature and the net baryon density \([p] + A[Fe]\). We can use eqn (2) to give one equation relating the temperature to the baryon density.

(b) Give the symbolic formula for the net baryon density\(^4\) at which half of the protons would have fused, in terms of \(K_{eq}\) and \(A\).

What can we use for the other equation relating temperature to baryon density? One of the fundamental constants in the Universe as it evolves is the baryon to photon

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\(^3\)The entropy cost for our reaction in reality depends upon the ratio of neutrons to protons. Calculations imply that this ratio falls out of equilibrium a bit earlier, and is about 1/7 during this period. By ignoring the difference between neutrons and protons, we avoid considering reactions of the form \(M p + (56 – M) n + (M – 26)e \rightarrow ^{56}\text{Fe}\).

\(^4\)Here we ask you to assume, unphysically, that all baryons are either free protons or in iron nuclei – ignoring the baryons forming helium and other elements. These other elements will be rare at early (hot) times, and rare again at late (cold) times, but will spread out the energy release from nucleosynthesis over a larger range than our one-reaction estimate would suggest.
number ratio. The total number of baryons has been conserved in accelerator experiments of much higher energy than those during nucleosynthesis. The cosmic microwave background (CMB) photons have mostly been traveling in straight lines\(^5\) since the *decoupling time*, a few hundred thousand years after the Big Bang when the electrons and nucleons combined into atoms and became transparent (decoupled from photons). The ratio of baryons to CMB photons \(\eta \sim 5 \times 10^{-10}\) has been constant since that point: two billion photons per nucleon\(^6\). Between the nucleosynthesis and decoupling eras, photons were created and scattered by matter, but there were so many more photons than baryons that the number of photons (and hence the baryon to photon ratio \(\eta\)) was still approximately constant.

We know the density of blackbody photons at a temperature \(T\); we integrate eqn (7.66) for the number of photons per unit frequency to get

\[
\rho_{\text{photons}}(T) = (2\zeta(3)/\pi^2)(k_B T/\hbar c)^3; \tag{3}
\]

the current density \(\rho_{\text{photons}}(T_{\text{CMB}})\) of microwave background photons at temperature \(T_{\text{CMB}} = 2.725\text{K}\) is thus a bit over 400 per cubic centimeter, and hence the current density of a fraction of a baryon per cubic meter.

(c) *Numerically matching your formula for the net baryon density at the halfway point in part (b) to \(\eta \rho_{\text{photons}}(T_{\text{reaction}})\), derive the temperature \(T_{\text{reaction}}\) at which our reaction would have occurred. (You can do this graphically, if needed.) Is it roughly a billion degrees Kelvin? Is the nucleon density roughly equal to that of air? (Hint: Air has a density of about 1 kg/m\(^3\).)*

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\(^5\)More precisely, they have traveled on geodesics in space-time.

\(^6\)It is amusing to note that this ratio is estimated using the models of nucleosynthesis that we are mimicking in this exercise.