Exercises

6.1 **Exponential atmosphere.**[1] [2] (Computation) ②

As you climb a mountain, the air becomes thin and cold, and typically rather windy. Are any of these effects due to equilibrium statistical mechanics? The wind is not; it is due to non-uniform heating and evaporation in far distant regions. We have determined that equilibrium statistical mechanics demands that two equilibrium bodies in contact must share the same temperature, even when one of them is above the other. But gas molecules fall down under gravity, ...

This example is studied in [41, I.40], where Feynman uses it to deduce much of classical equilibrium statistical mechanics. Let us reproduce his argument. Download our molecular dynamics software [10] from the text web site [129] and the hints for this exercise. Simulate an ideal gas in a box with reflecting walls, under the influence of gravity. Since the ideal gas has no internal equilibration, the simulation will start in an equilibrium ensemble at temperature T.

(a) *Does the distribution visually appear statistically stationary? How is it possible to maintain a static distribution of heights, even though all the atoms are continuously accelerating downward? After running for a while, plot a histogram of the height distribution and velocity distribution. Do these distributions remain time independent, apart from statistical fluctuations? Do their forms agree with the predicted equilibrium Boltzmann distributions?*

The equilibrium thermal distribution is time independent even if there are no collisions to keep things in equilibrium. The number of atoms passing a plane at constant z from top to bottom must match the number of atoms passing from bottom to top. There are more atoms at the bottom, but many of them do not have the vertical kinetic energy to make it high enough.

Macroscopically, we can use the ideal gas law ($PV = Nk_BT$, so $P(z) = \rho(z)k_BT$) to deduce the Boltzmann distribution giving the density dependence on height.[3]

(b) *The pressure increases with depth due to the increasing weight of the air above. What is the force due to gravity on a slab of thickness Δz and area A? What is the change in pressure from z to $z - \Delta z$? Use this, and the ideal gas law, to find the density dependence on height. Does it agree with the Boltzmann distribution?*

Feynman then deduces the momentum distribution of the particles from the balancing of upward and downward particle fluxes we saw in part (a). He starts by arguing that the equilibrium probability ρ_v that a given atom has a particular vertical velocity v_z is independent of height.[4] (The atoms at different heights are all at the same temperature, and only differ in their overall density; since they do not interact, they do not know the density, hence

[1] From *Statistical Mechanics: Entropy, Order Parameters, and Complexity* by James P. Sethna, copyright Oxford University Press, 2007, page 124. A pdf of the text is available at pages.physics.cornell.edu/sethna/StatMech/ (select the picture of the text). Hyperlinks from this exercise into the text will work if the latter PDF is downloaded into the same directory/folder as this PDF.

[2] This exercise and the associated software were developed in collaboration with Christopher Myers.

[3] Feynman then notes that this macroscopic argument can be used for any external force! If F is the force on each atom, then in equilibrium the pressure must vary to balance the external force density $F\rho$. Hence the change in pressure $F\rho\, \mathrm{d}x = \mathrm{d}P = \mathrm{d}(k_BT\rho) = k_BT\, \mathrm{d}\rho$. If the force is the gradient of a potential $U(\mathbf{x})$, then picking a local coordinate x along the gradient of U we have $-\nabla U = F = k_BT(\mathrm{d}\rho/\mathrm{d}x)/\rho = k_BT(\mathrm{d}\log\rho)/\mathrm{d}x = k_BT\nabla\log\rho$. Hence $\log\rho = C - U/k_BT$ and $\rho \propto \exp(-U/k_BT)$. Feynman then makes the leap from the ideal gas (with no internal potential energy) to interacting systems...

[4] At this point in the text, we already know the formula giving the velocity distribution of a classical system, and we know it is independent of position. But Feynman, remember, is re-deriving everything from scratch. Also, be warned: ρ in part (b) was the mass density; here we use it for the probability density.

the atom's velocity distribution cannot depend on z).

(c) *If the unknown velocity distribution is $\rho_v(v_z)$, use it and the Boltzmann height distribution deduced in part (b) to write the joint equilibrium probability distribution $\rho(v_z, z, t)$.*

Now consider[5] the atoms with vertical velocity v_z in a slab of gas of area A between z and $z + \Delta z$ at time t. Their probability density (per unit vertical velocity) is $\rho(v_z, z, t) A \Delta z$. After a time Δt, this slab will have accelerated to $v_z - g\Delta t$, and risen a distance $h + v_z \Delta t$, so

$$\rho(v_z, z, t) = \rho(v_z - g\Delta t, z + v_z \Delta t, t + \Delta t). \quad (1)$$

(d) *Using the fact that $\rho(v_z, z, t)$ is time independent in equilibrium, write a relation between $\partial\rho/\partial v_z$ and $\partial\rho/\partial z$. Using your result from part (c), derive the equilibrium velocity distribution for the ideal gas.*

Feynman then argues that interactions and collisions will not change the velocity distribution.

(e) *Simulate an interacting gas in a box with reflecting walls, under the influence of gravity. Use a temperature and a density for which there is a layer of liquid at the bottom (just like water in a glass). Plot the height distribution (which should show clear interaction effects) and the momentum distribution. Use the latter to determine the temperature; do the interactions indeed not distort the momentum distribution?*

What about the atoms which evaporate from the fluid? Only the very most energetic atoms can leave the liquid to become gas molecules. They must, however, use up every bit of their extra energy (on average) to depart; their kinetic energy distribution is precisely the same as that of the liquid.[6]

Feynman concludes his chapter by pointing out that the predictions resulting from the classical Boltzmann distribution, although they describe many properties well, do not match experiments on the specific heats of gases, foreshadowing the need for quantum mechanics.[7]

[5] Feynman gives a complicated argument avoiding partial derivatives and gently introducing probability distributions, which becomes cleaner if we just embrace the math.

[6] Ignoring quantum mechanics.

[7] Quantum mechanics is important for the internal vibrations within molecules, which absorb energy as the gas is heated. Quantum effects are not so important for the pressure and other properties of gases, which are dominated by the molecular center-of-mass motions.