PHYS 114, Seminar 8, "A New Demon Algorithm" Presentation, 28 March 2018

(i) To refresh our memory, Maxwell's demon is a thought experiment in which James Clark Maxwell proposed how the second law of thermodynamics might hypothetically be violated by a small "demon" that controls a tiny door between two chambers of gas The demon quickly opens and closes the door as the gas molecules approach, so that only the fast molecules pass into the other chamber while the slow molecules remain in the original chamber. In essence, the demon causes one chamber to heat up while the other cools down (because faster molecules are hotter). This would cause entropy to decrease, which violates the second law that total entropy can never decrease over time for an isolated system.

The chemical demon algorithm, or generalized demon algorithm, is a generalization of the demon algorithm we looked at in Chapter 4. In this case, the demon carries two sacks, one for energy and the other for particles. Originally, when considering the exchange of energy, we could find the probability of the demon having energy E_d with the Boltzmann distribution. Now, our demon can exchange both energy and particles with the system, so the probability that the demon has energy E_d and N_d particles is given by the Gibbs distribution (Eq. 4.142)

$$\text{Eq. 7.13:} \quad P(E_d, N_d) = \frac{1}{Z_G} e^{-\beta(E_d - \mu N_d)}$$

where Z_G is the grand canonical partition function. We are thinking of the demon as a system that exchanges energy and particles with a reservoir at constant T and μ.

(ii) Beginning with the result for a 3D semiclassical system with noninteracting particles, $\mu = -kT \ln[Z(T,V,1)/N]$, adapt to a 1D chemical potential and show that with $k=1$, $h=1$, and $m = 1/2$, a Demon simulation should give:

$$\mu = -T \ln\left[\frac{L}{N}\sqrt{\pi T}\right]$$

Start with Eq. 7.8, which says the chemical potential is the change in free energy of the system due to the addition of a particle...

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \approx F_{N+1} - F_N = -kT \ln\left(\frac{Z_{N+1}}{Z_N}\right)$$

The partition function of an N particle system is:

$Z_N = \sum_s e^{-\beta E_s}$, where E_s is the energy of microstate s with N particles.

Similarly...

$Z_{N+1} = \sum_{s,r} e^{-\beta E_{s,r}}$, where the sum over r is over all possible coordinates and momenta of the added particle, and $E_{s,r}$ is the energy when N particles are in state s and added particle is in state r.

Rewriting the argument of our ln function...

$$\frac{Z_{N+1}}{Z_N} = \frac{\sum_{s,r} e^{-\beta \Delta E_{s,r}} e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}, \text{ where } \Delta E_{s,r} = E_{s,r} - E_s$$

However, we are told our particles are noninteracting, so $\Delta E_{s,r}$ does not depend on s. The sum over s in the numerator cancels with the one in the denominator, and the sum over r becomes an integral over the position and momentum of the added particle.

We want to find our chemical potential in 1D, so we are only looking at a dimension of length L...

$\mu = -kT \ln\left[\frac{L}{N} \int e^{-\beta E_r} \frac{dp}{h}\right]$, where the $\frac{1}{N}$ factor comes from particles being indistinguishable.

Using method from beginning of Chapter 6, we can evaluate this integral and set $k=1$, $h=1$, and $m = 1/2$...

$$\mu = -kT \ln\left(\frac{L}{N}(2\pi m kT)^{1/2} \frac{1}{h}\right)$$

$$\therefore \mu = -T \ln\left(\frac{L}{N}\sqrt{\pi T}\right), \text{ as desired.}$$

(iii) G&T 7.7: The chemical potential of a 1D ideal gas

Program "ChemicalDemon" = implements chemical demon algorithm in which demon exchanges particles and energy with system

(a) Assume chemical demon exchanges particles and energy with 1D ideal gas.
Parameters (default): $N = 100$, $E = 200$, $L = 100$

Units: $\Delta x \Delta p = 1$ and $m = 1/2$, so particle energy $\epsilon = p^2$; in other words, energy and momenta are integers ($p_{max} = \sqrt{E}$)

N particles placed in phase space lattice with no more than 1 particle in a cell such that the desired E_{tot} is achieved.

Initial demon parameters: $E_d = 0$, $N_d = 0$

Qualitative features? Where are most of the particles located?

It appears as though, in our p vs. x graph, the particles are evenly spread (approximately) along the x-axis.

Run for different E values. What does p vs. x look like now?

Higher values of E cause there to be more clumping around the x-axis with more variation in momentum space. Lower values of E cause the converse to happen.

(b) Explain why simulation is identical to that of ideal gas in the semiclassical limit. Show that $\mu = -T\ln\left(\frac{L}{N}\sqrt{\pi T}\right)$.

We did this in part (ii)! For sake of details, note the semiclassical limit is that in which particles will remain indistinguishable, even in the limit of high temperatures, which is the quantum mechanical treatment.

(c) Use default ($N=100$, $E=200$, $L=100$) and run for 200 Monte Carlo steps per particle (mcs) for equilibration. "Reset Averages" and average over at least 1000 mcs.

Plot of $\ln P(E_d, N_d = 1)$ vs. E_d is approximately linear for small E_d. Slope of the line should be $\frac{1}{T}$.

Plot of $\ln P(E_d = 1, N_d)$ vs. N_d gives us a slope of $\frac{\mu}{T}$.

Theoretically, we get $\mu = -T\ln\left(\frac{L}{N}\sqrt{\pi T}\right)$, which gives us $\mu = 1.2$ which concurs with experimental μ being approximately 2.

Extra notes after meeting with Amy...

★ More particles should cause slope $1/T$ ($\ln P(E_d)$ vs. E_d) to be larger

★ Work for last part of 7.7...

Use Data Tool → Measure slope

$P \ln(E_d)$ vs E_d : slope $= \frac{1}{T} = 0.24 \rightarrow T \cong 4$

$P \ln(N_d)$ vs. N_d : slope $= \frac{\mu}{T} \approx 1.1$

Plug T into theory... $\mu = -T \ln(\sqrt{\pi T})$ $(L = N = 100)$

$$-\frac{\mu}{T} = \ln\left(\sqrt{4\pi}\right) \approx 1.3$$

Our slope is quite close using the simulation!

★ $\mu \equiv$ Gibbs free energy per particle

★ μ should become more negative with attractive particles

$$\mu = \mu_{ideal} + \underbrace{\mu_{inter}}_{= -kT \langle e^{-\beta U} \rangle}$$

Attractive particles → negative U → positive exponential; Negative coeffs, so overall result will be negative and μ of system should decrease

★ hard core interaction ≡ no two particles can be in the same spatial position

★ attractive well ≡ square well