# Chemical Demon Algorithm

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# Algorithm Setup

## Demon interacting with bath of fixed T, μ - will obey Gibbs distribution

(depiction very inaccurate)

Bath

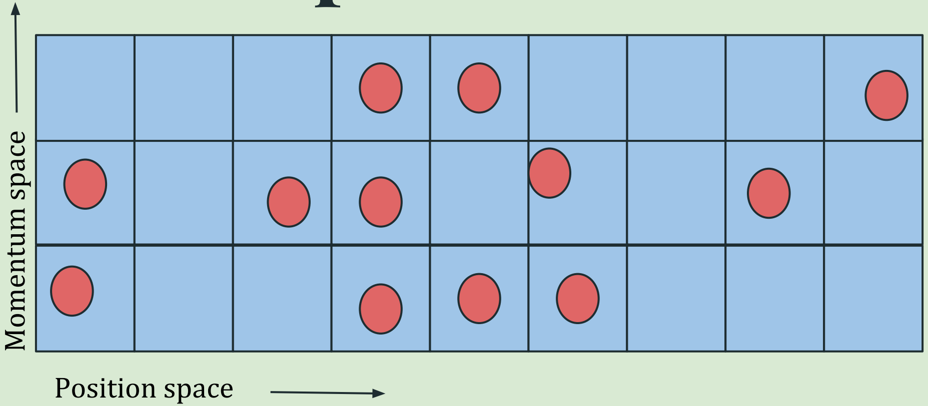
- 1-dimensional bath with discrete array of positions x and momenta p (two-dimensional phase space)
- Particles randomly assigned to lattice spots, max 1 particle/spot

Demon

- Demon with a "bag of energy" $E_d$ and particles $N_d$
- Interacts with one particle at a time, if it has enough energy

Probability distribution: P_d = e^(-beta( $E_d$ -mu* $N_d$))/Z_G

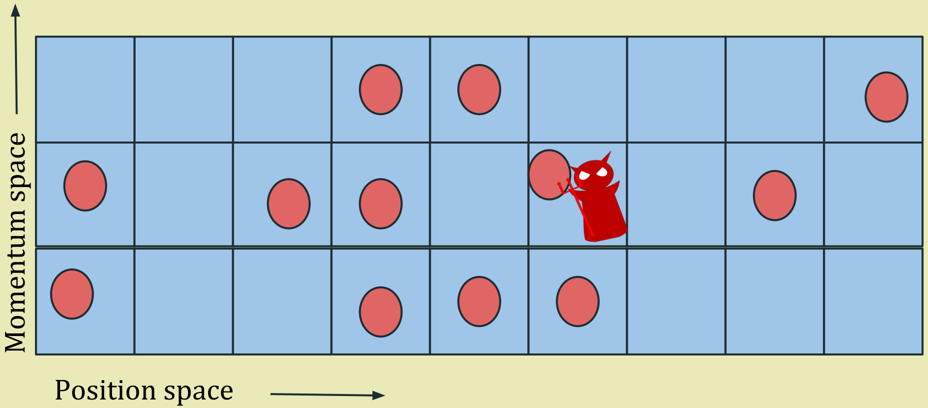
# Initial particle distribution




Create an initial setup with randomly distributed particles N and total energy E.

Initially, demon energy $E_d$ is zero and number of particle $N_d$ is zero.

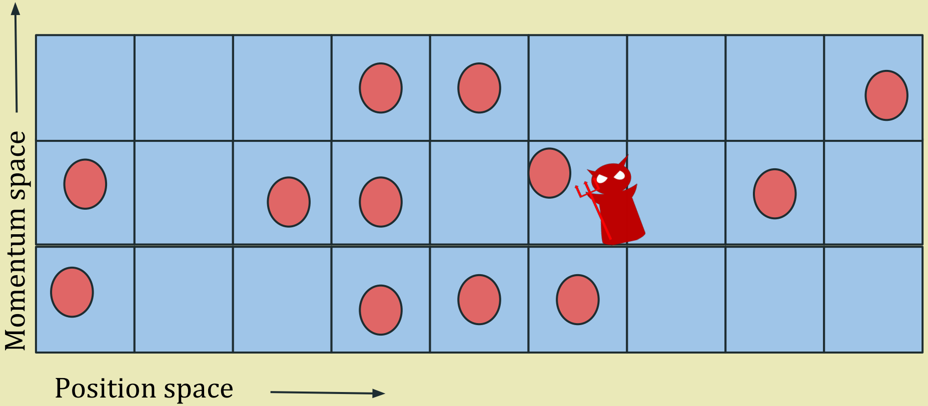
# Interaction with bath




Demon moves to a random **phase-space** lattice point.

**Case 1. If there is a particle**, calculate change in energy ΔE to remove it.

# Interaction with bath

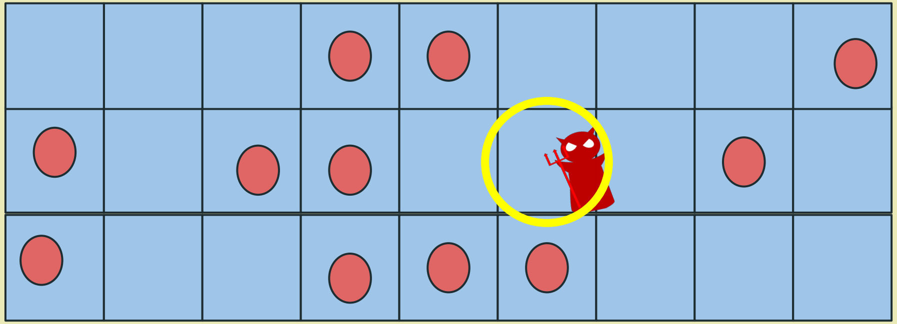



Demon moves to a random **phase-space** lattice point.

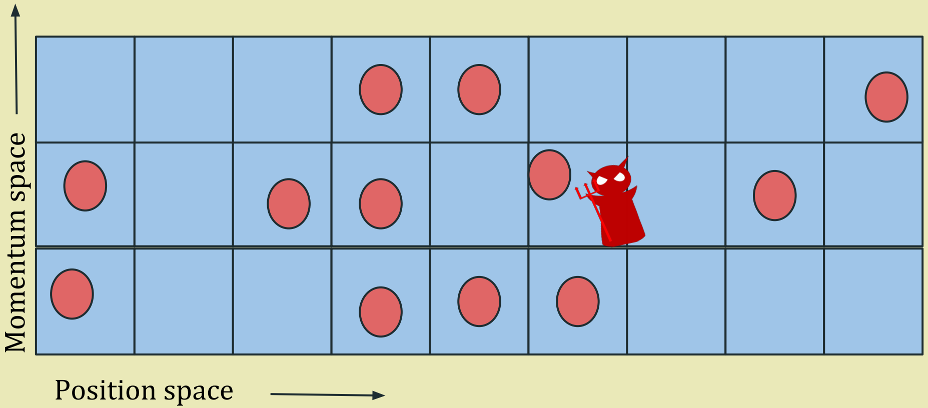
**Case 1. If there is a particle**, calculate change in energy $\Delta E$ to remove it.

If $\Delta E < E_d$ (demon has enough energy) then:

1. $E_d \rightarrow E_d - \Delta E$
2. $N_d \rightarrow N_d + 1$
3. Remove particle from lattice



# Interaction with bath



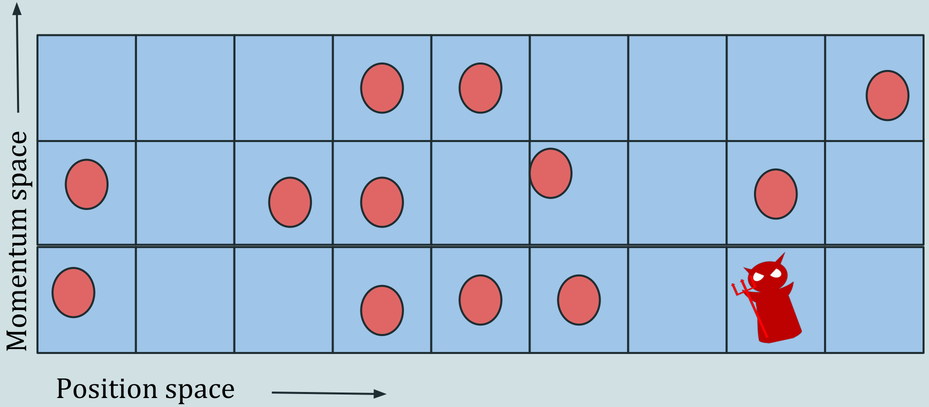

Demon moves to a random **phase-space** lattice point.

**Case 1. If there is a particle**, calculate change in energy ΔE to remove it.

If the demon does not have enough energy:
No changes to $E_d$ or $N_d$

In either case: Record the new configuration of $E_d$ and $N_{d,}$ and the probability
P_d = e^(-beta( $E_d$ -mu* $N_d$))/Z_G

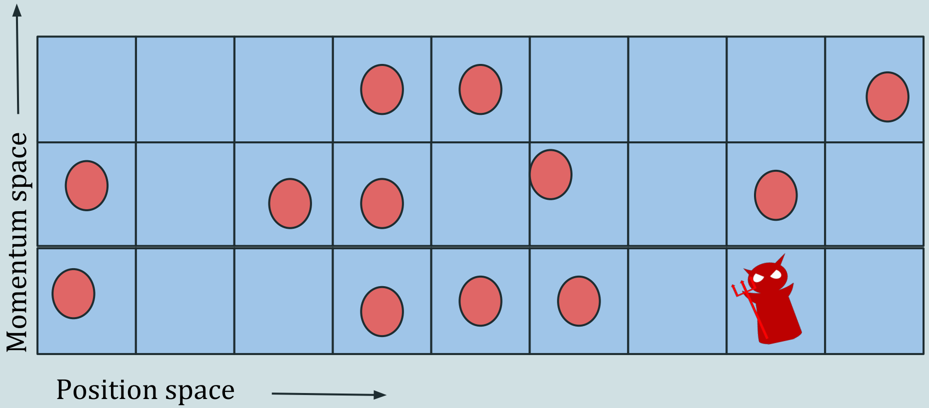
# Interaction with bath




**Case 2.** If there is **no particle** in the space:

Calculate the energy needed to add a particle to the space.

# Interaction with bath

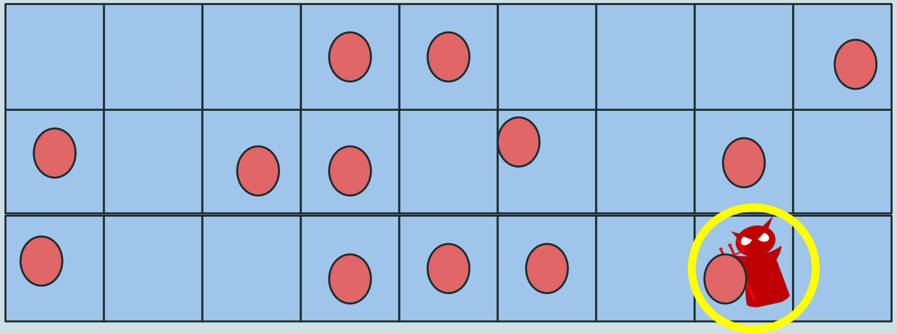



**Case 2.** If there is **no particle** in the space:

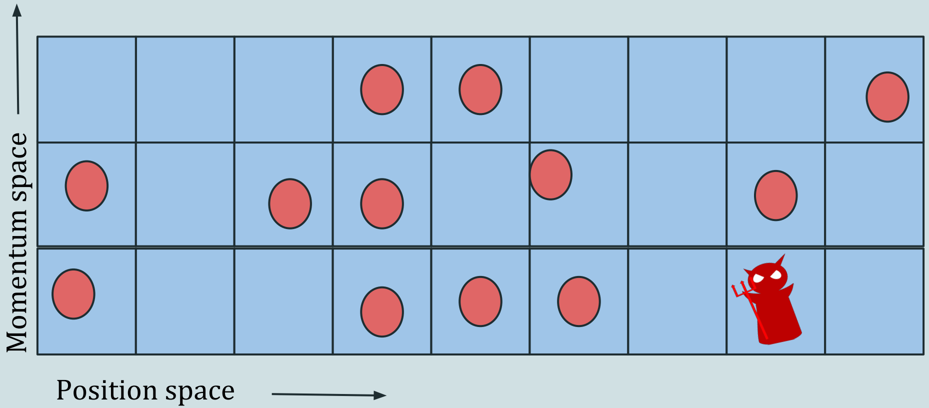
Calculate the energy needed to add a particle to the space.

If $\Delta E < E_d$ (demon has enough energy) then:

1. $E_d \rightarrow E_d - \Delta E$
2. $N_d \rightarrow N_d - 1$
3. Add particle to lattice



# Interaction with bath




**Case 2.** If there is **no particle** in the space:

Calculate the energy needed to add a particle to the space.

If the demon doesn't have enough energy

No change to energy, particles, etc. of demon or lattice, no change to configuration

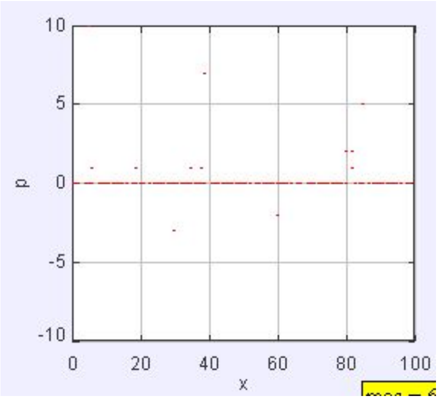
In either case: Record the new configuration of $E_d$ and $N_d$, and the probability P_d = e^(-beta( $E_d$ -mu* $N_d$))/Z_G

# Trying some simulations!

(depiction also inaccurate)

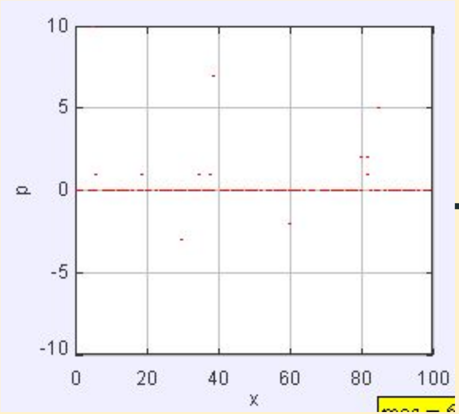
Initial settings:

1. N = 100, E = 200, and L = 100
2. p = √(2mE), i.e. non-interactive moving particles
3. Maximum p = √E
   (implies m = ½ as p = √(2mE))
4. $E_d$ and $N_d$ both initially zero

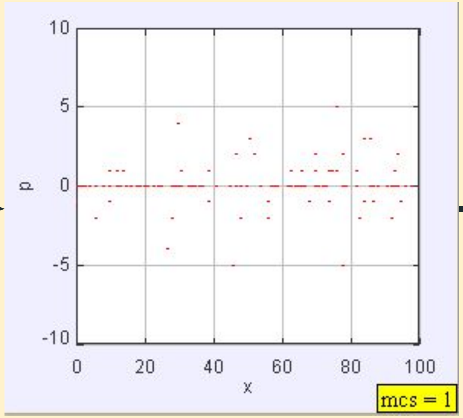



Initial phase space distribution is chosen to agree with N = 100 and E = 200.

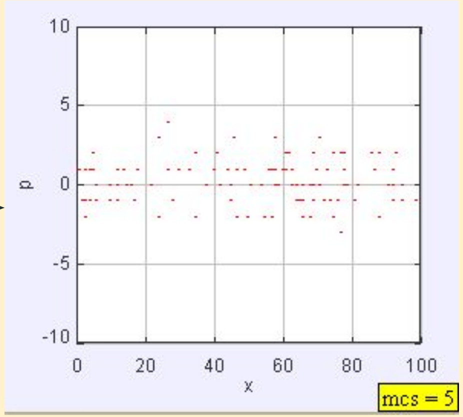
# Simulations: Qualitative Observations in Phase Space




Initial state




Some spread into higher p




Equilibrium distribution

1. Particle distribution is even in x, as for an ideal gas no distinction in energy between particles at a certain position
2. Some particles share position but no overlap in phase space is allowed (similar to semiclassical gas model)
3. Spread in p around p = 0 with fewer particles at larger p values

# Simulations: Predicting the value of the chemical potential

$$\mu = -kT \ln(Z(T, V, 1)/N)$$

To find the partition function for a single particle:

$$Z = \sum_n e^{-\beta \epsilon_n}$$

From quantum model of particle in a box:

$$\epsilon_n = \frac{n^2 h^2}{8mL^2} \equiv \frac{\alpha^2}{\beta}$$

$$\alpha^2 = \frac{\beta h^2}{8mL^2}$$

Re-express Z:

$$Z = \sum_{n=1}^{\infty} e^{-\alpha^2 n^2} = \sum_{n=0}^{\infty} e^{-\alpha^2 n^2} - 1$$

Convert to Gaussian integral:

$$Z = \frac{1}{\alpha} \int_0^{\infty} (e^{-u^2} du) - 1$$

# Simulations: Predicting the value of the chemical potential

$$\mu = -kT\ln(Z(T,V,1)/N)$$

$$Z = \frac{1}{\alpha}\int_0^\infty (e^{-u^2}du) - 1$$

Evaluate Gaussian integral:

$$Z = L\left(\frac{2\pi m}{\beta h^2}\right)^{1/2} - 1 \approx L\left(\frac{2\pi m}{\beta h^2}\right)^{1/2}$$

Evaluate chemical potential with
h = 1, k = 1, m = ½

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

# Simulations: Relating the chemical potential to distributions

$$\mu = -kT\ln(Z(T,V,1)/N)$$

Probability of some state: $$P_s = \frac{1}{Z_G}e^{-\beta(E_s-\mu N_s)}$$

Partial derivatives:

$$\left(\frac{\partial \ln P_s}{\partial E_d}\right)\Bigg|_{N=1} = -\frac{1}{kT}$$

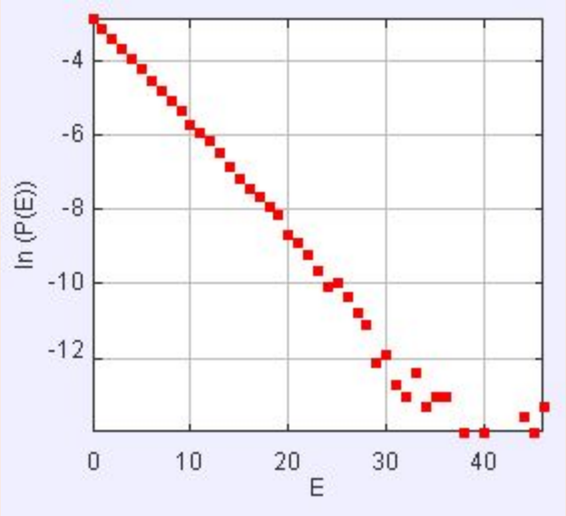
$$\left(\frac{\partial \ln P_s}{\partial N_d}\right)\Bigg|_{E=1} = \frac{\mu}{kT}$$

Linear slopes

# Simulations: Quantitative analysis

- Look at phase space distribution averages after equilibrium is achieved using n ~ 1000 MC steps

**Energy distribution averages**




$$\left(\frac{\partial \ln P_s}{\partial E_d}\right)\Bigg|_{N=1} = -\frac{1}{kT}$$

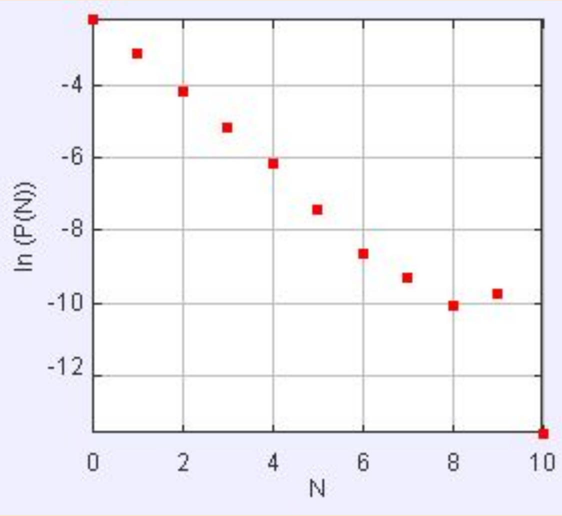
Slope = -1/kT = -1/T

Value m = -0.6 → T = 5/3

# Simulations: Quantitative analysis

- Look at phase space distribution averages after equilibrium is achieved using n ~ 1000 MC steps

**Number distribution averages**




$$\left(\frac{\partial \ln P_s}{\partial N_d}\right)\Bigg|_{E=1} = \frac{\mu}{kT}$$

Slope = - 2 = μ/T where T = 5/3 (approximate)

μ = -6/5 = -1.2 (approximately)


Pretty similar?

**Compare:** $\mu = -T \ln\left(\frac{L}{N}\sqrt{\pi T}\right)$

$$\mu = -\frac{5}{3}\ln\left(\frac{100}{100}\sqrt{5\pi/3}\right) = -1.379$$

# Conclusions

- A model of ideal gas particles in the semi-classical limit agrees with the demon algorithm
- Demon algorithm provides negative chemical potential in agreement with the following equation, where the partition function is taken from semi-classical ideal gas:

$$\mu = -kT \ln(Z(T, V, 1)/N)$$