

Monte Carlo for particle systems

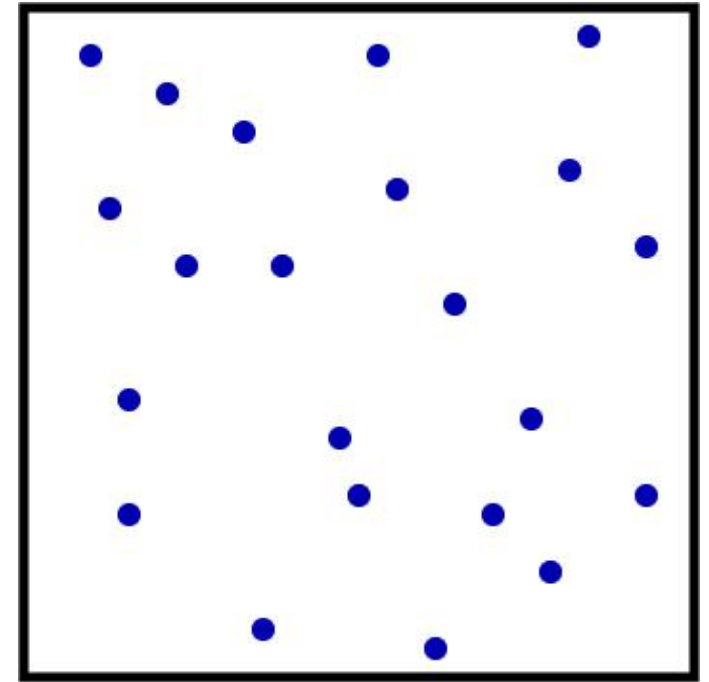
Interacting molecules in a volume

$$\langle A \rangle = \frac{1}{Z} \int \prod_{i=1}^N dx_i^d A(\{x_i\}) e^{-E(\{x_i\})/k_B T}$$

$$Z = \int \prod_{i=1}^N dx_i^d e^{-E(\{x_i\})/k_B T}$$

We will consider simple spherical particles (atoms)

$$E(\{x_i\}) = \sum_{i=1}^N U(\vec{x}_i) + \sum_{i \neq j} V(\vec{x}_i, \vec{x}_j)$$



$V=V(r)$; spherically symmetric. More complicated molecules involve more difficult energy calculations

Long-range interactions (e.g. Coulomb) lead to N^2 scaling of the computational effort (CPU time).

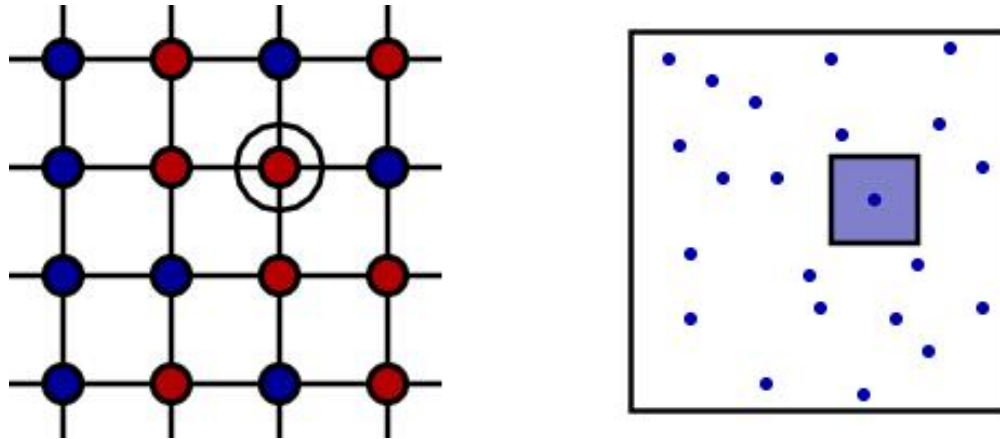
Lennard-Jones (e.g., for noble gases):
- can be truncated

$$V(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$

Metropolis Monte Carlo scheme

Principle same as in Ising simulation; update involves

- selecting a particle at random
- attempt to move it within a box
- calculate energy change (more complicated than Ising)



Adjust the window so that the acceptance rate is close to 50%

Typically periodic boundary conditions are used

```
x1=x0+delta*rand(-0.5:0.5)
if x1 < 0; x1=x1+ll; end
if x1 > ll; x1=x1-ll; end
y1=y0+delta*rand(-0.5:0.5)
if y1 < 0; y1=y1+ll; end
if y1 > ll; y1=y1-ll; end
```

Adjust the window size during equilibration

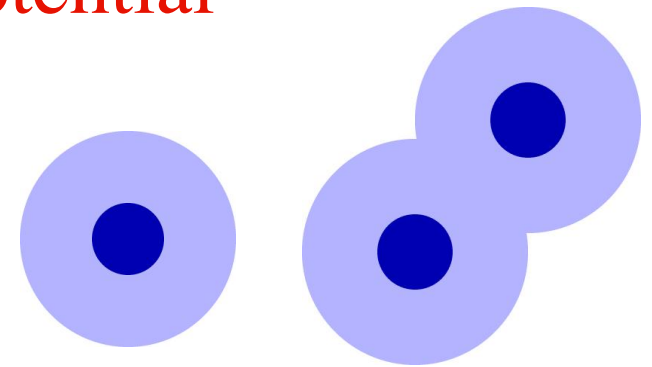
- e.g., 20 times in total

```
function adjustedelta(steps,accepted,delta,ll)
    arate=accepted/steps
    if arate < 0.4; delta=delta/1.5; end
    if arate > 0.6 && delta < ll/4; delta=delta*1.5; end
    return delta
end
```

Example: "atoms" with a simplified potential

N particles in periodic 3D box of length L

$$V(r) = \begin{cases} \infty, & r \leq r_1 \\ -V, & r_1 < r \leq r_2 \\ 0, & r > r_2 \end{cases} \quad \text{"collision"}$$



Energy = -V times number of "overlapping" particle pairs

-counting overlaps is expensive, $\sim N^2$

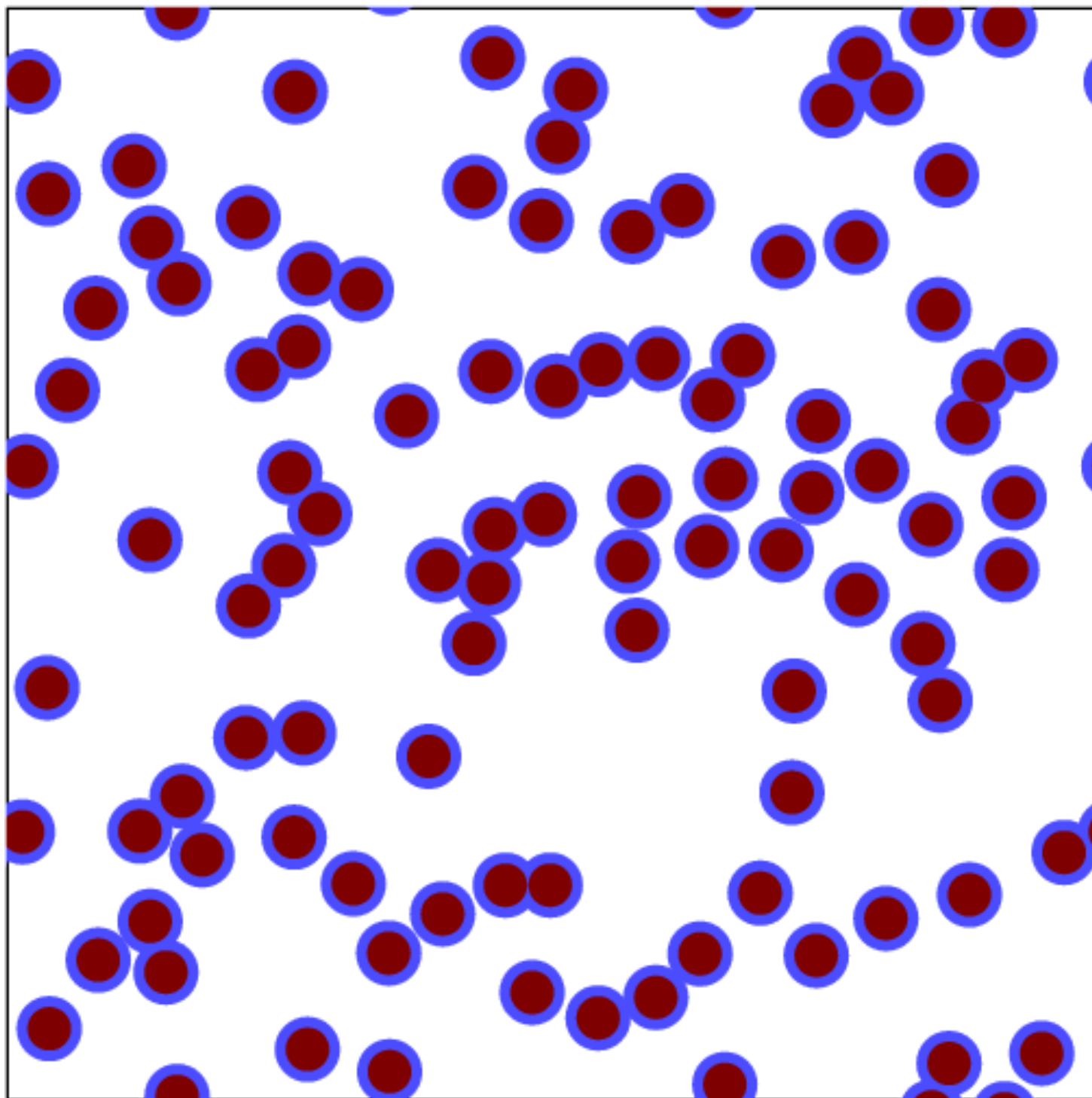
-some tricks with list of "neighbors" to reduce time

MC step

```
for j=1:n
    x0=xyz[1,j]; y0=xyz[2,j]; z0=xyz[3,j]
    x1,y1,z1=newcoordinates(ll,delta,x0,y0,z0)
    violate=false # will later be true if "collison"
    n1=0 # number of overlapping pairs
    for i=1:n # count overlaps, terminate loop if violation
        if i==j continue
        dx=abs(x1-xyz[1,i]); dx=min(dx,ll-dx)
        dy=abs(y1-xyz[2,i]); dy=min(dy,ll-dy)
        dz=abs(z1-xyz[3,i]); dz=min(dz,ll-dz)
        r2=dx^2+dy^2+dz^2
        if r2 < r2_1
            violate=true # violation found
            break # not allowed, terminate loop
        elseif r2 < r2_2
            n1=n1+1
        end
    end
    end
    if violate; continue; end # terminate update if violation
    if rand() < exp(v0*(n1-n0[j])/temp)
        xyz[1,j]=x1; xyz[2,j]=y1; xyz[3,j]=z1
        n0[j]=n1 # save new number of overlaps for particle j
        accepted=accepted+1
    end
end
end
```

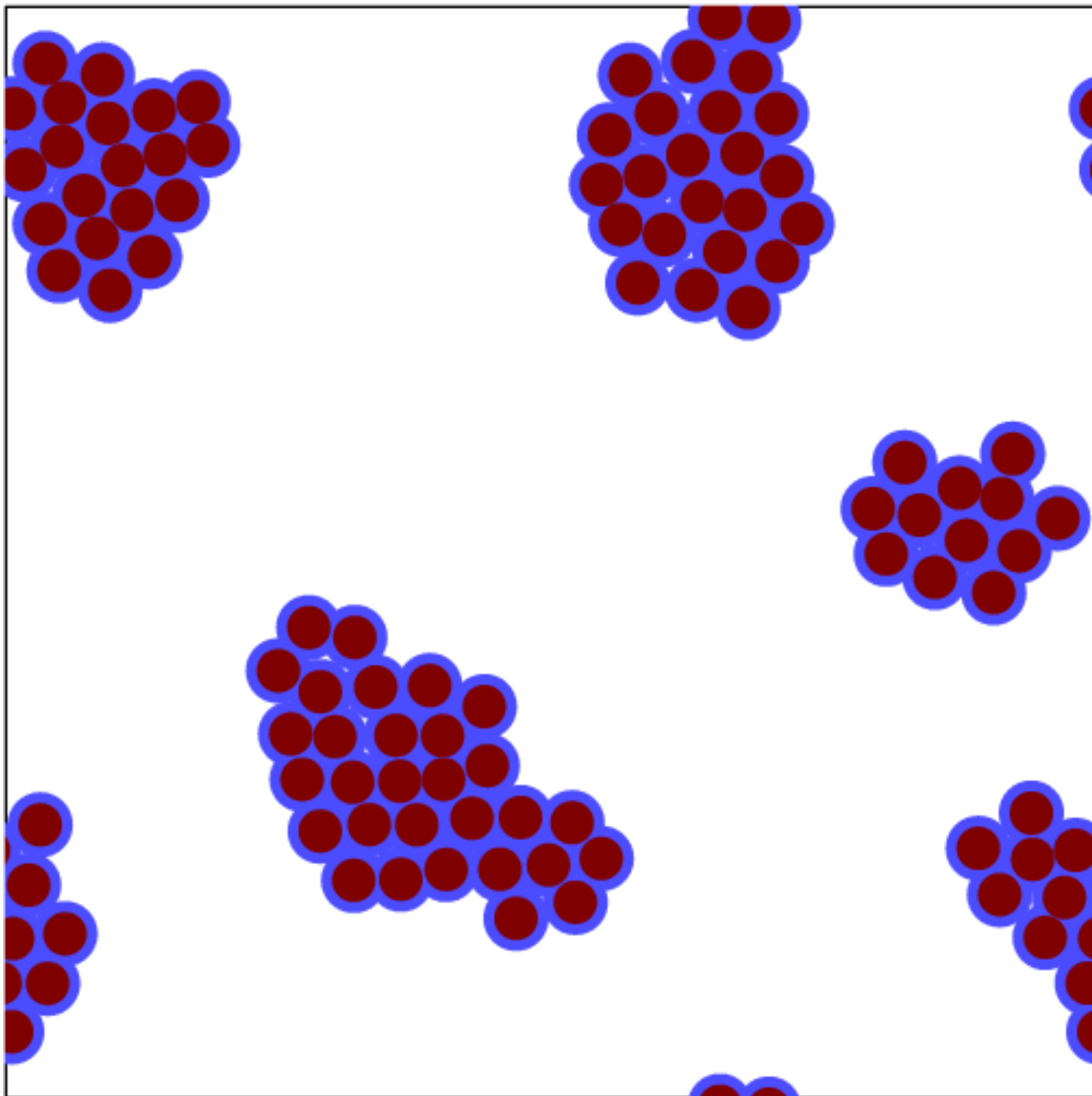
$T = 1.00$

1



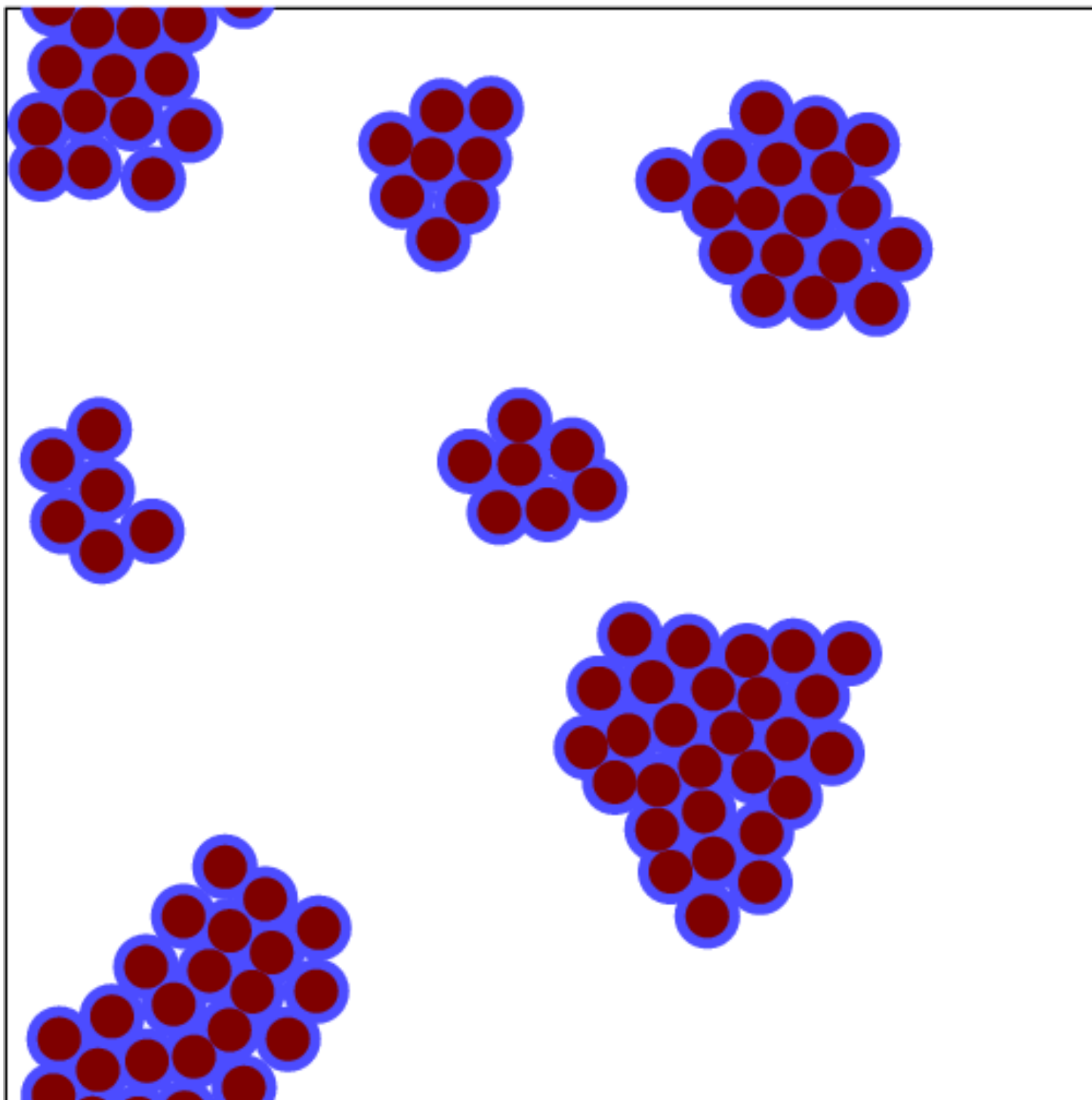
$T = 0.20$

10



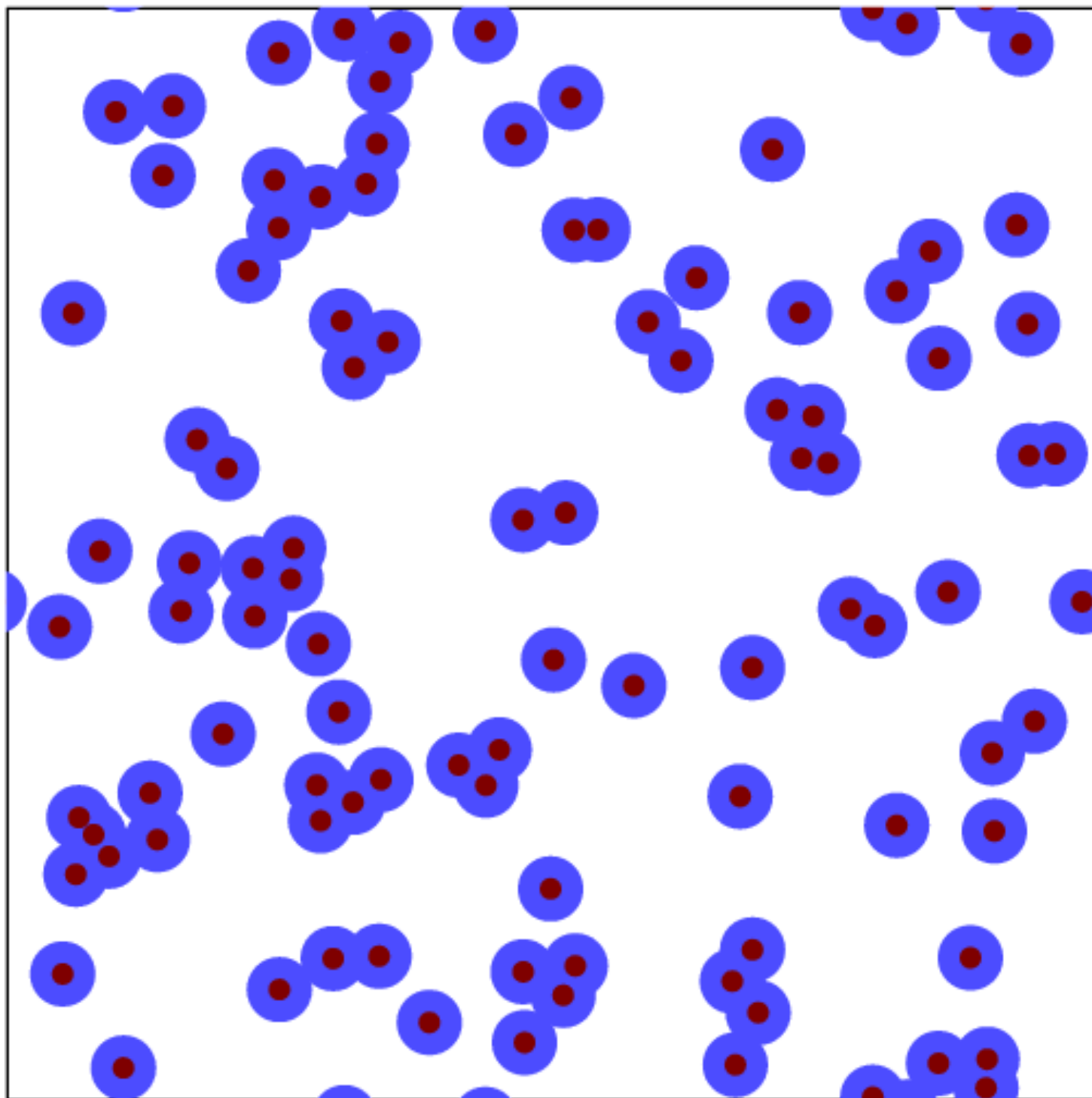
$T = 0.20$

1000



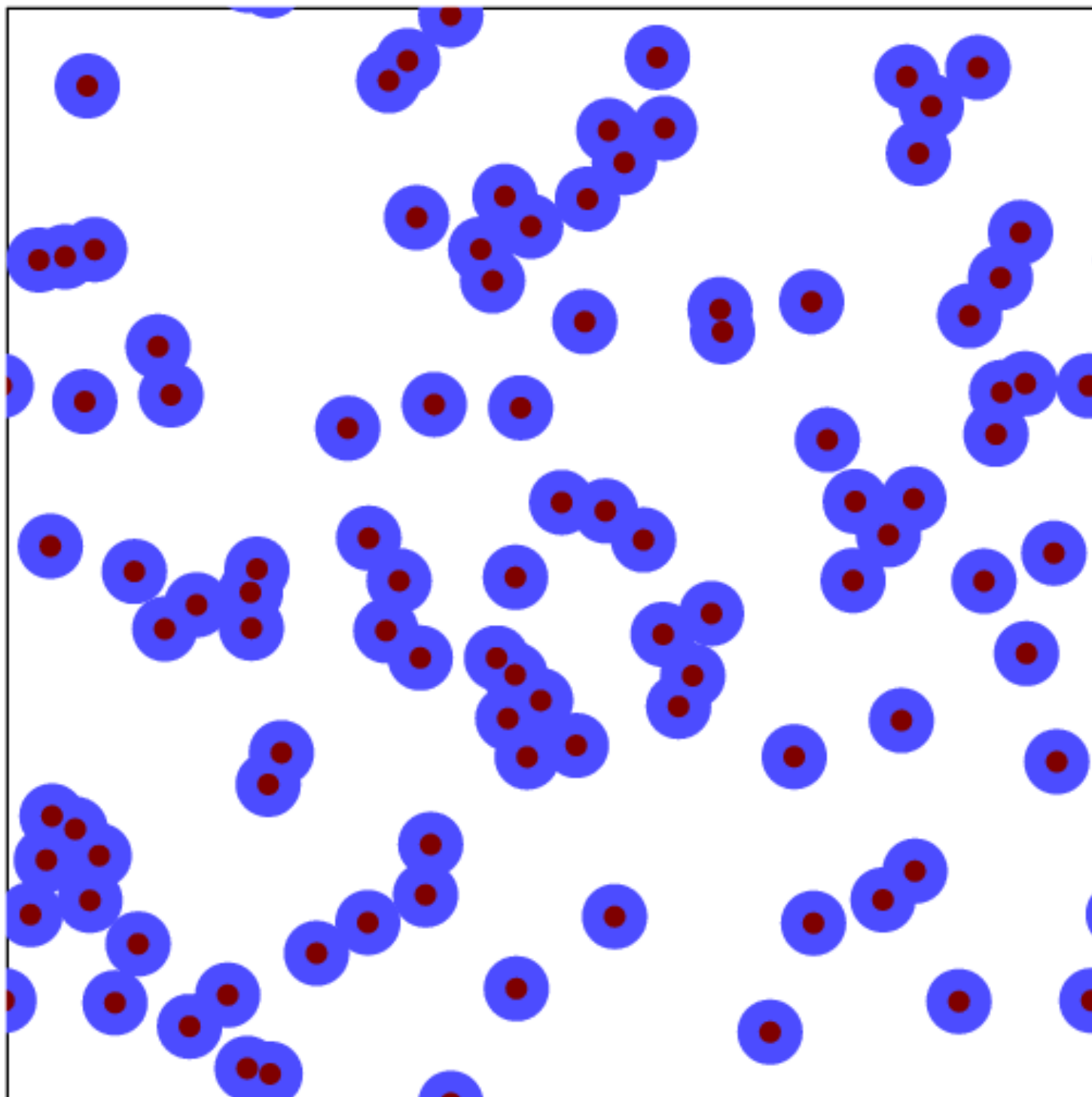
$T = 5.00$

5



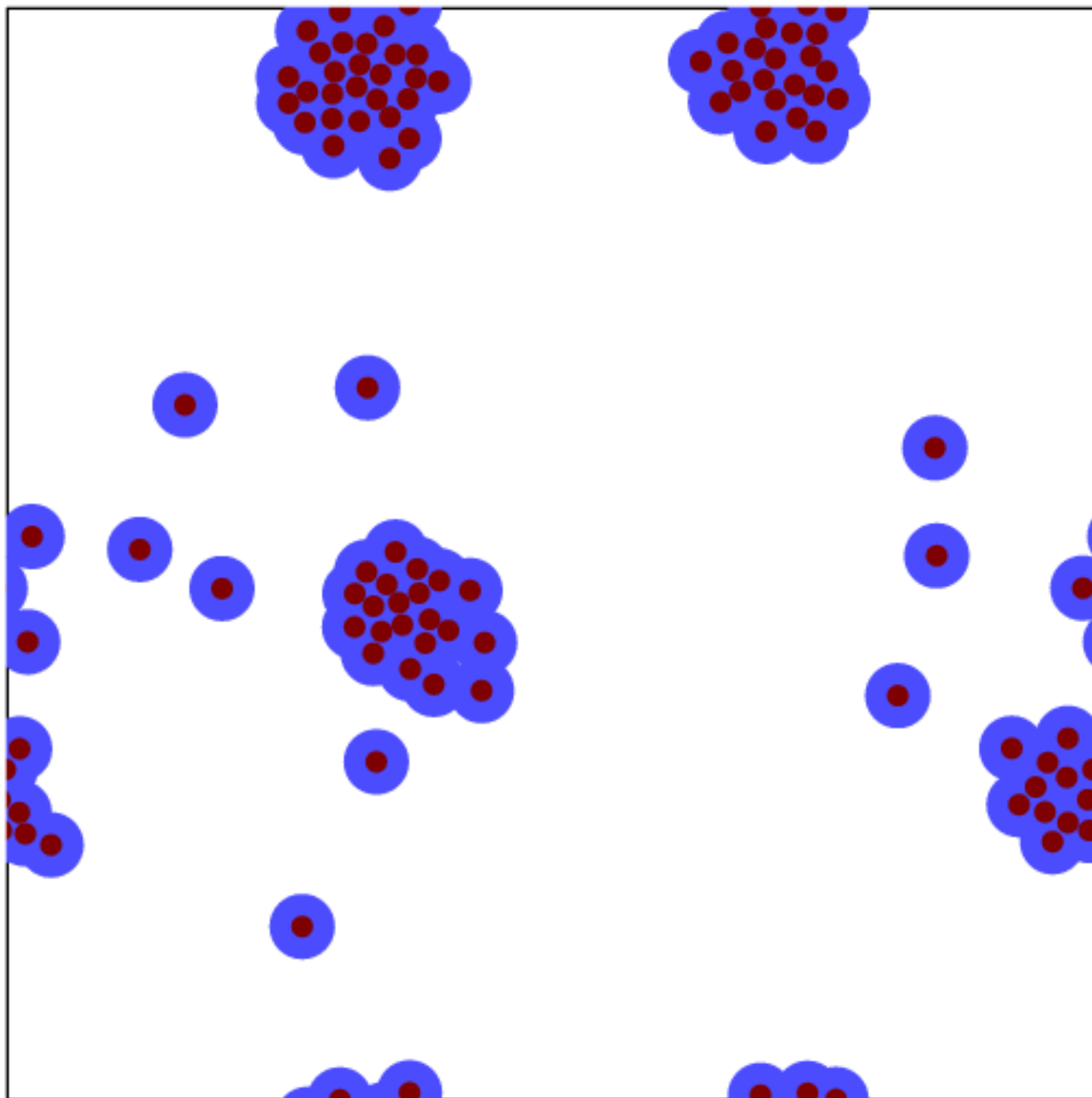
$T = 1.00$

5

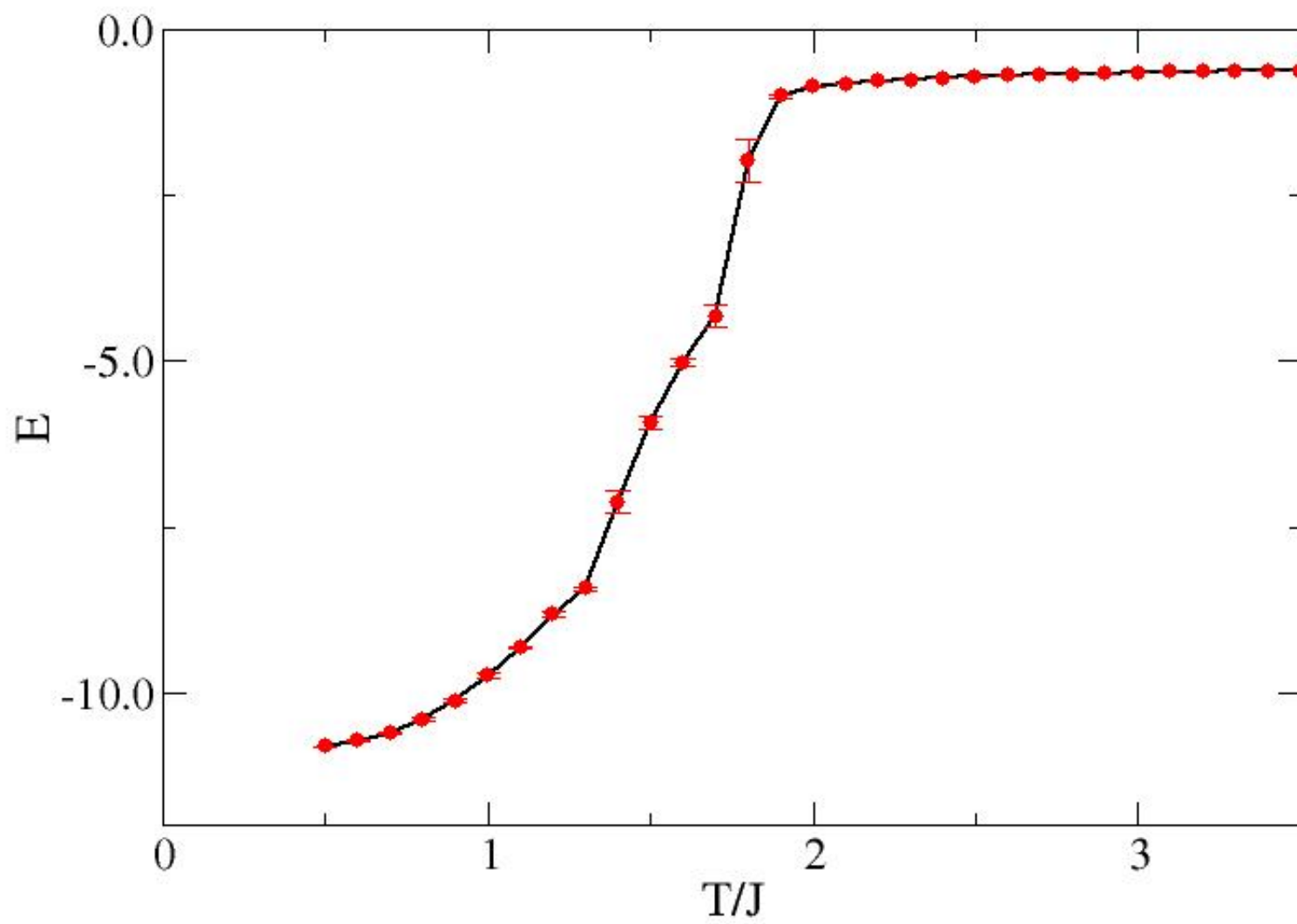


$T = 1.00$

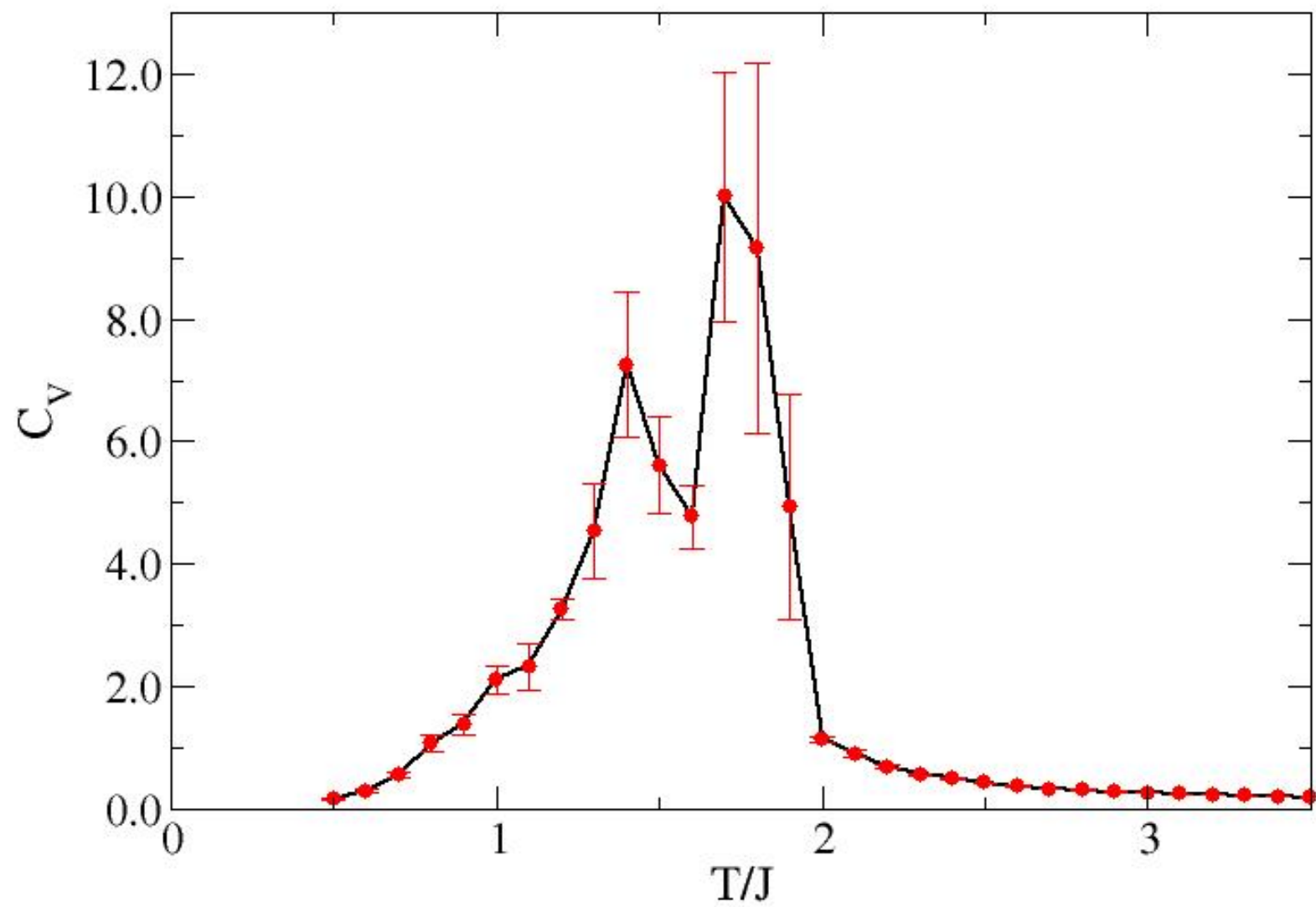
1000



Internal energy



Specific heat



Simulated annealing

General, very useful optimization method

In optimization, some function of a number of variables is to be minimized or maximized.

In many systems one can think of this function (or its negative value) as an energy of a many-body system.

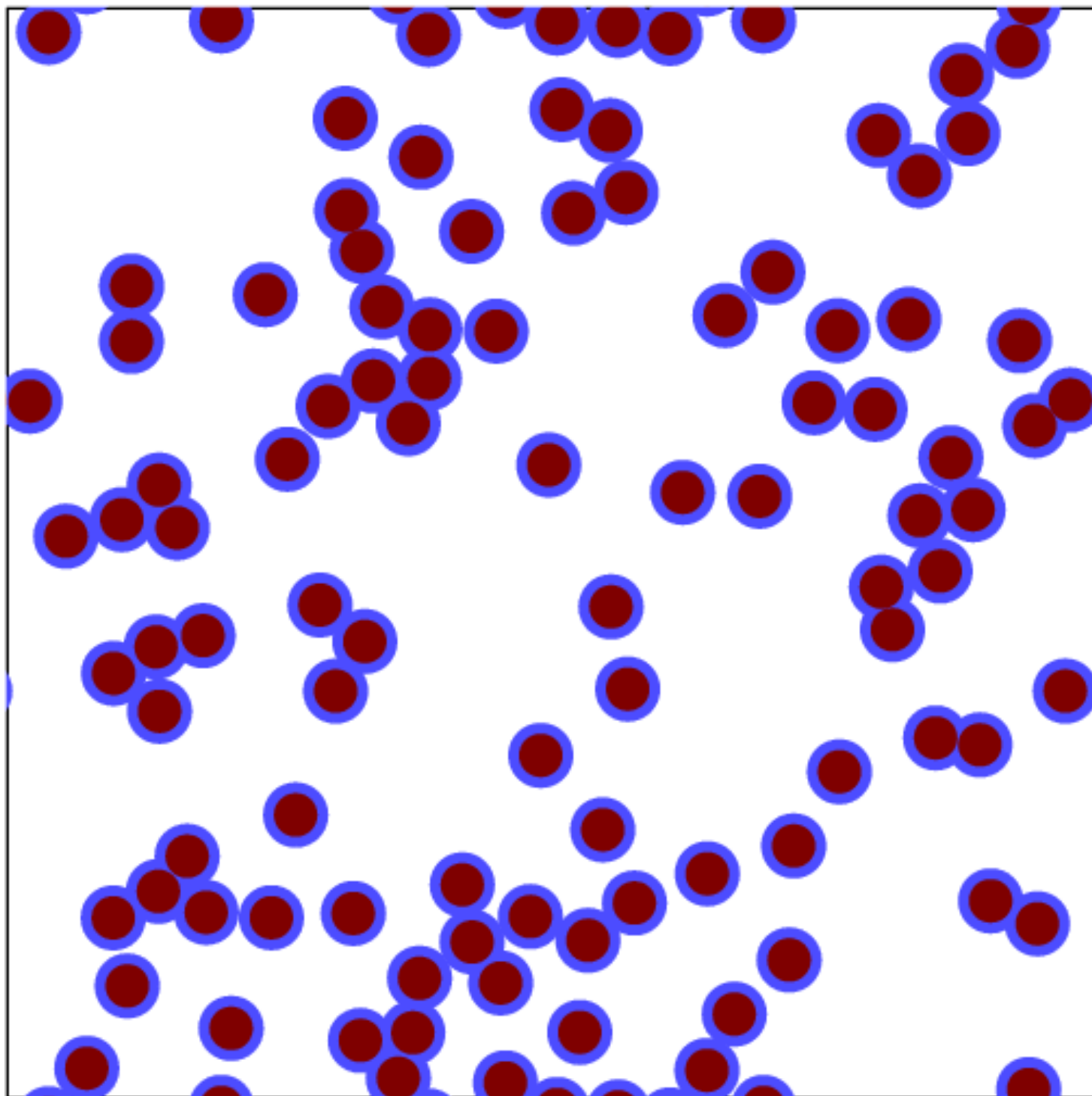
Introduce a fictitious temperature

Minimize E in a Monte Carlo simulation with slowly decreasing temperature.

May not give the absolutely best solution within finite time, but typically a very good solution is obtained.

$T = 0.99$

100



$T = 0.99$

1000

