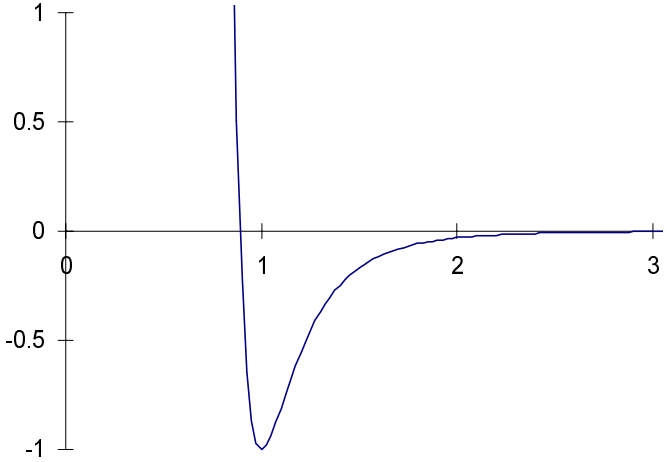
Introduction

Study small clusters of atoms:

- N = 2 to 14, and 50 atoms
- Interaction via a pair-wise Lennard-Jones potential



- Zero pressure (i.e. no collisions with other clusters)
- Thermal equilibrium

Find:

- Energy as a function of N and T
- Boiling point as a function of N
- Mechanism of cluster boiling

Monte Carlo Simulations

Use Metropolis Algorithm

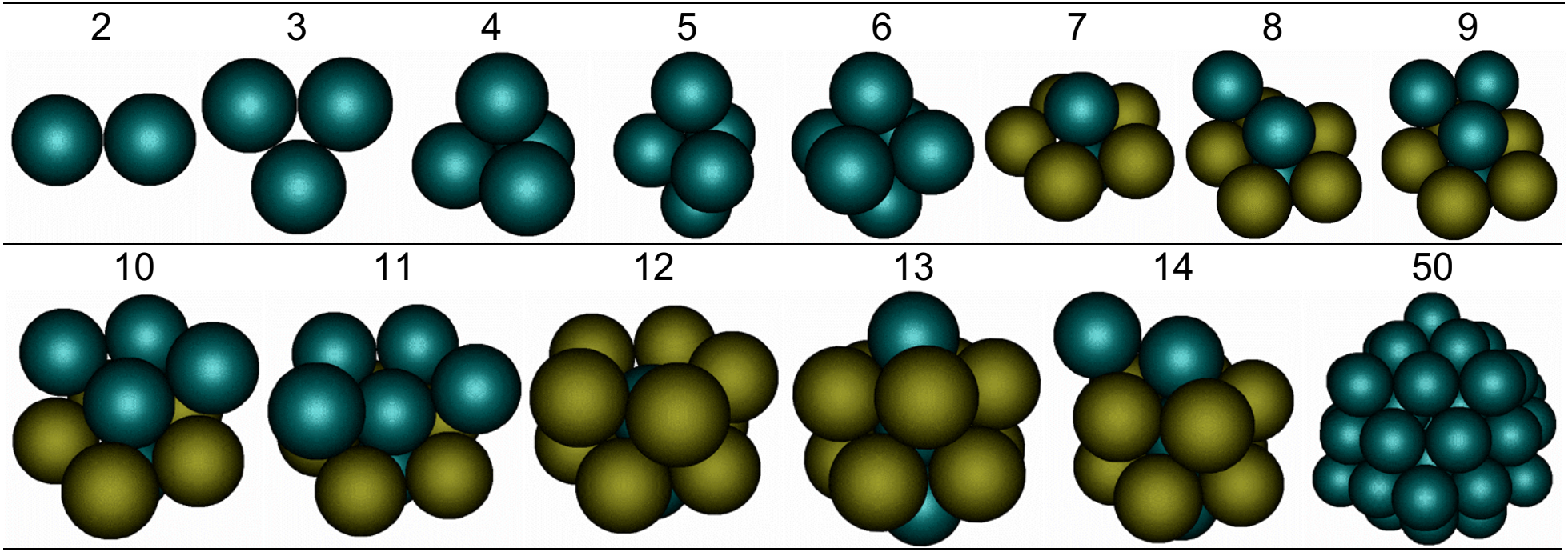
- **Move set**: Move a single atom by a normal deviate with standard deviation 0.04
- **Equilibration**: 0.1 million steps per atom of exponential cooling from T=1 to T=0.005, then 0.5 million steps per atom at the desired temperature
- **Data collection**: 0.5 million steps per atom, 10 independent restarts

Zero temperature simulations (energy minimization)

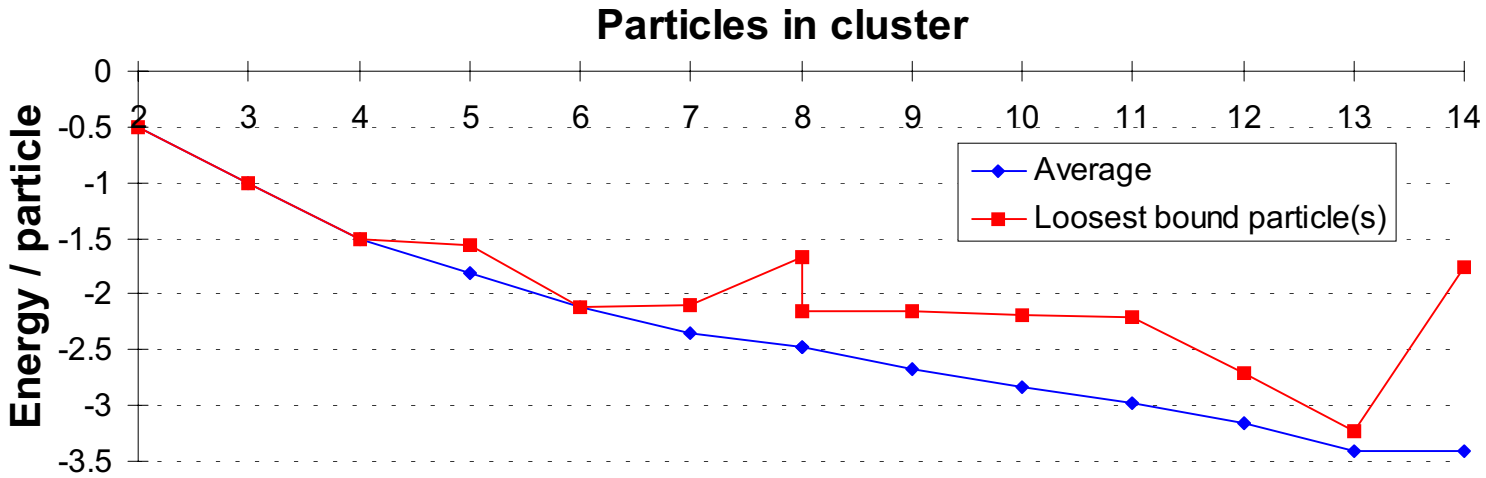
- **50 independent restarts** of Metropolis algorithm at T=0.0001
- **"Polishing" solutions** by moving particles down energy gradient
- Take the lowest energy solution found

4 billion Monte Carlo steps total, 100 hours computation time !

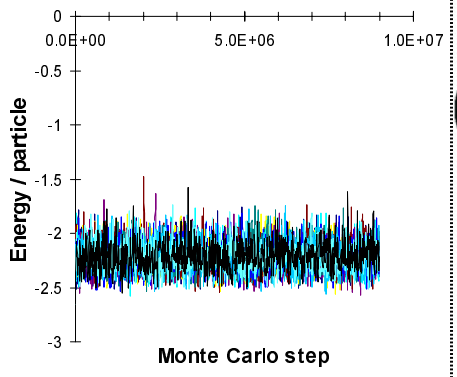
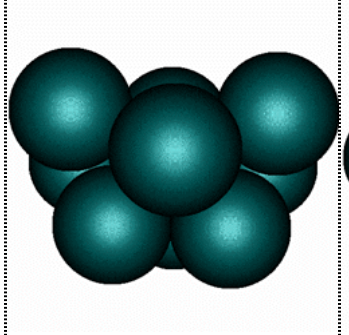
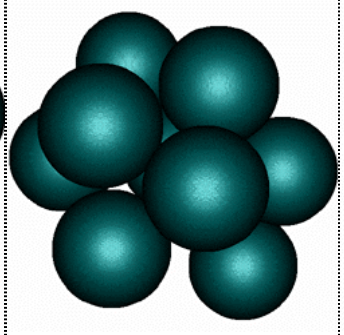
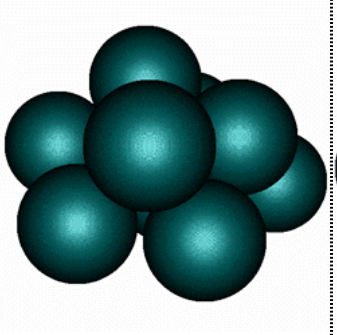
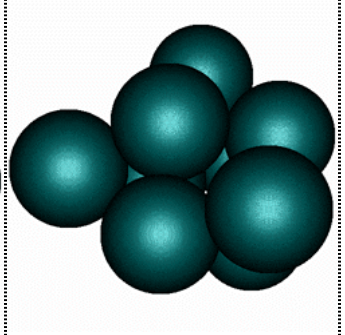
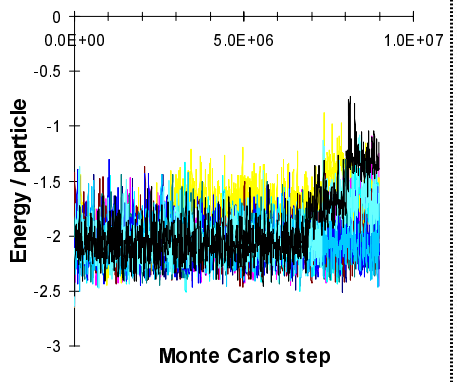
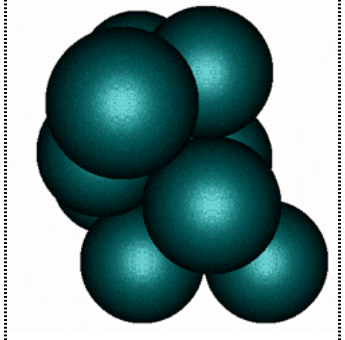
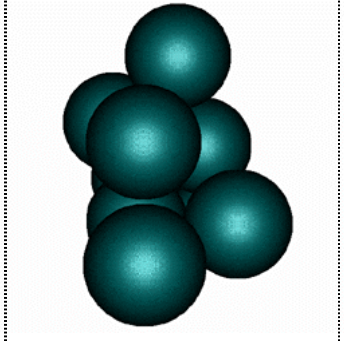
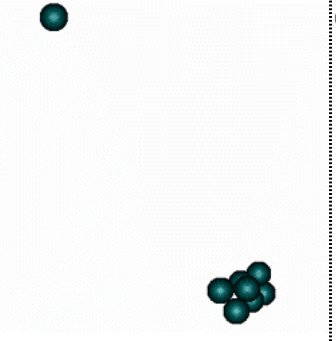
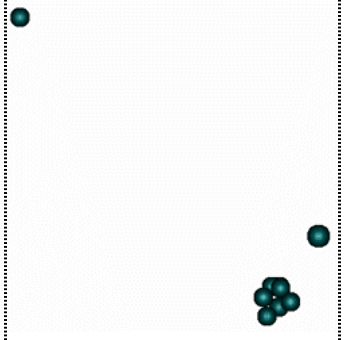
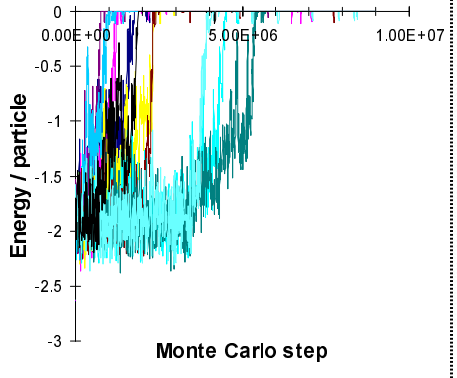
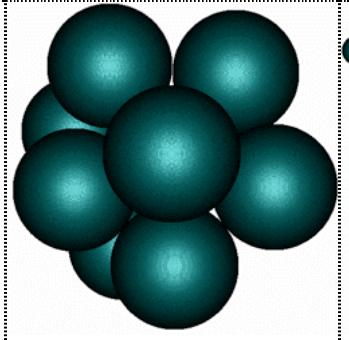
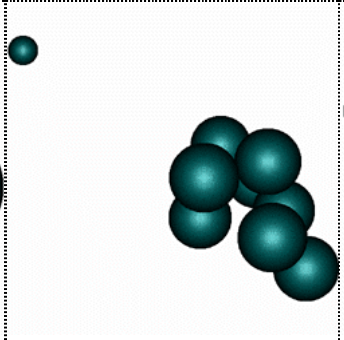
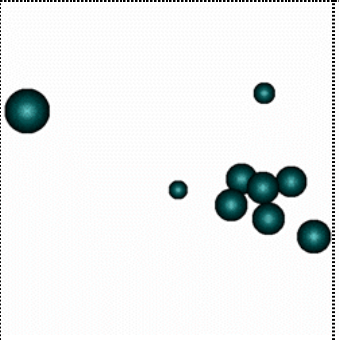
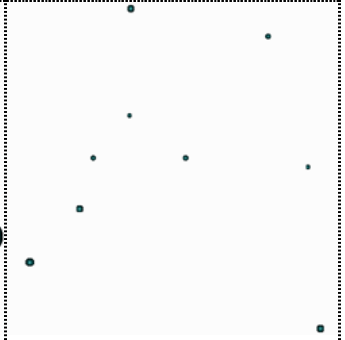
Ground States of Lennard-Jones Clusters



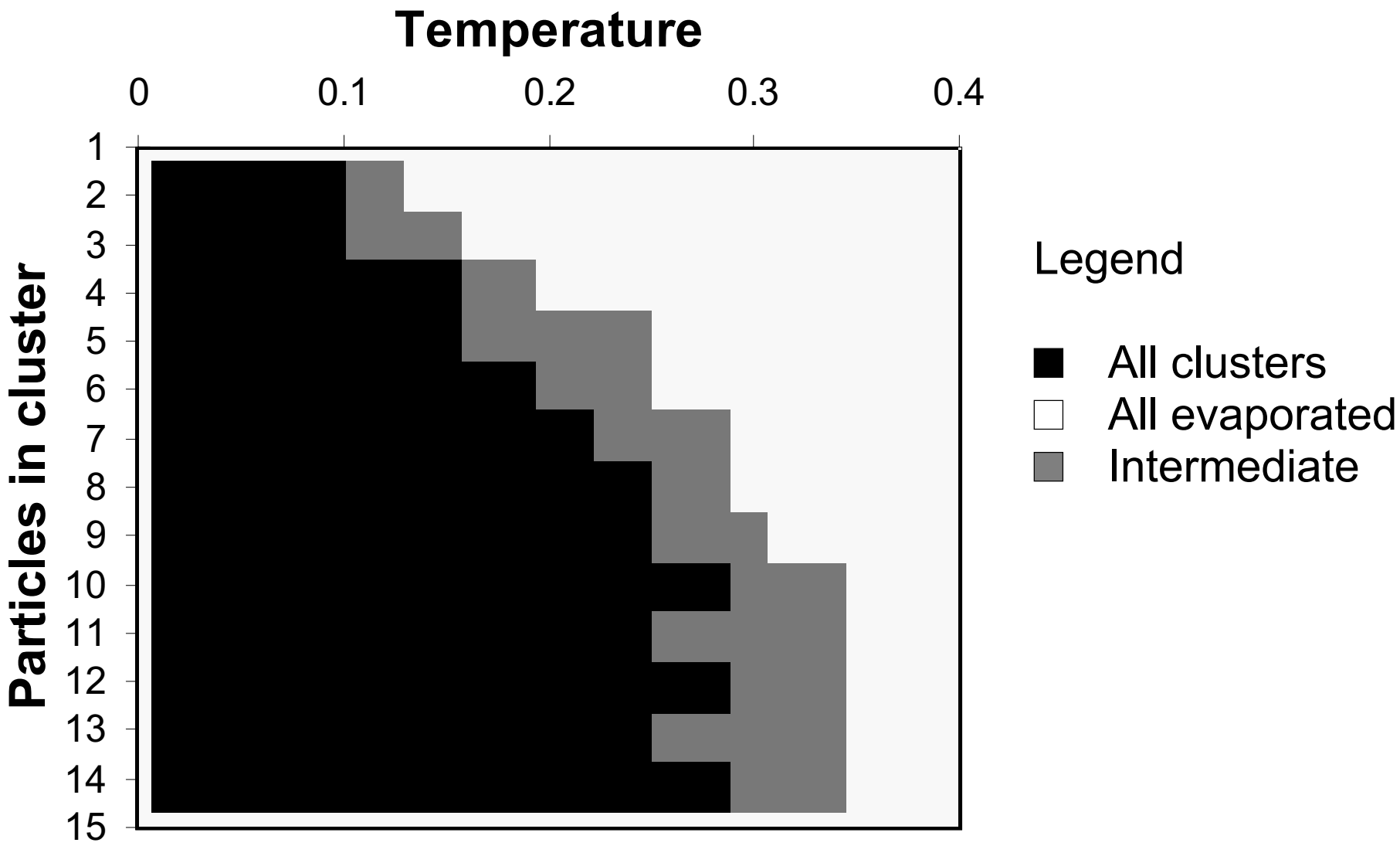
Gold spheres lie at the vertices of a planar pentagon



The Approach to Thermal Equilibrium

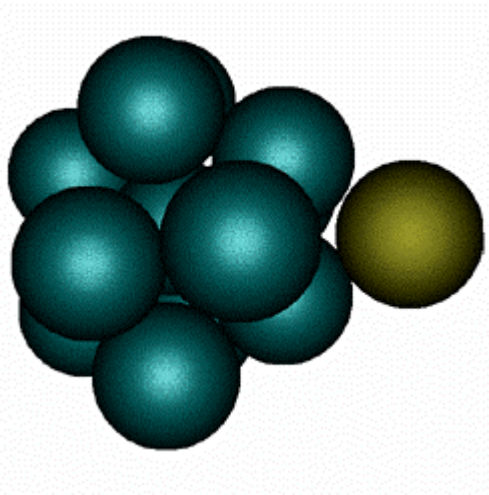
Temp.	Energy(time)	Snapshots from a Monte Carlo run (black line in graphs)			
0.23					
		0 steps	2.7 mil. steps	6.3 mil. steps	9 mil. Steps
0.28					
		0 steps	6.3 mil. steps	7.2 mil. steps	8.1 mil. steps
0.33					
		0 steps	0.9 mil. steps	1.8 mil. steps	2.7 mil. steps

Stability of Clusters

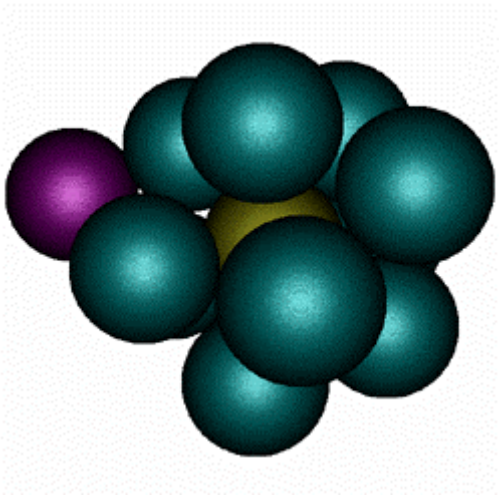


Atoms “Feel” Average Binding Energy

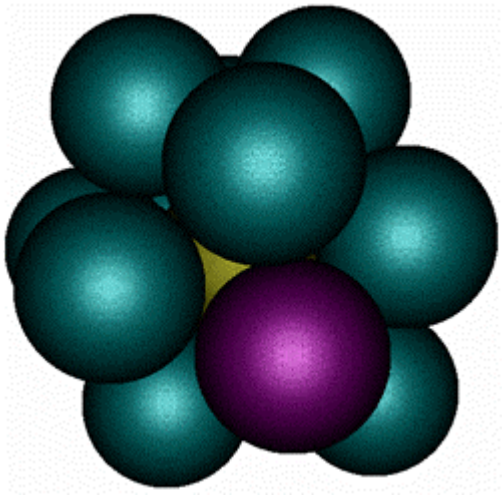
Weakly bound atoms (gold in the first frame, and purple in the next) do not stay weakly bound:



1.4 million steps



2.8 million steps



4.2 million steps

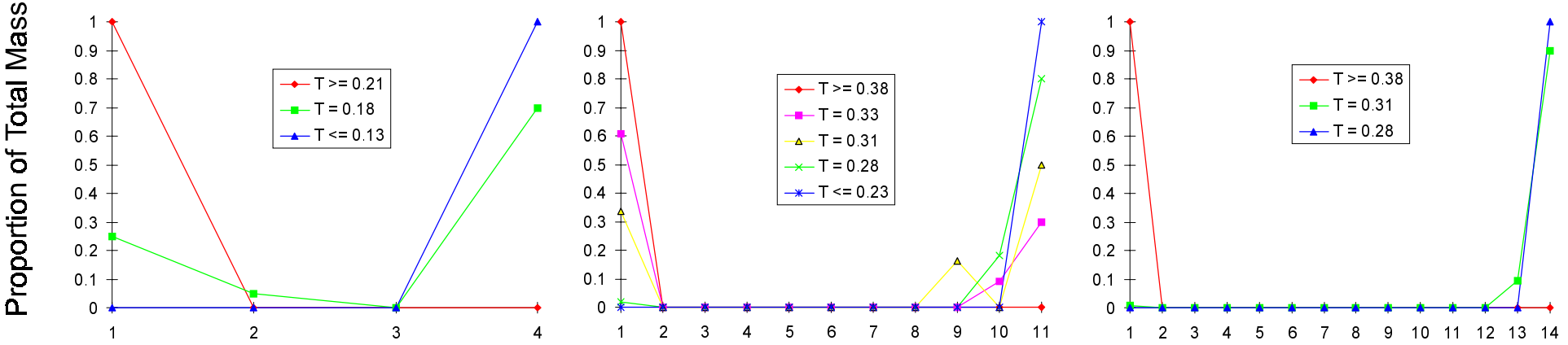
N=14, T=0.28

Thus, particles “feel” the average binding energy, so this parameter affects the boiling temperature more than the energy of the weakest bond.

Complete Evaporation Occurs Rapidly After One Particle Leaves

- During a simulation, most clusters are completely intact, completely dissociated, or have one or two particles dissociated
- Few intermediate stages seen because they occur quickly

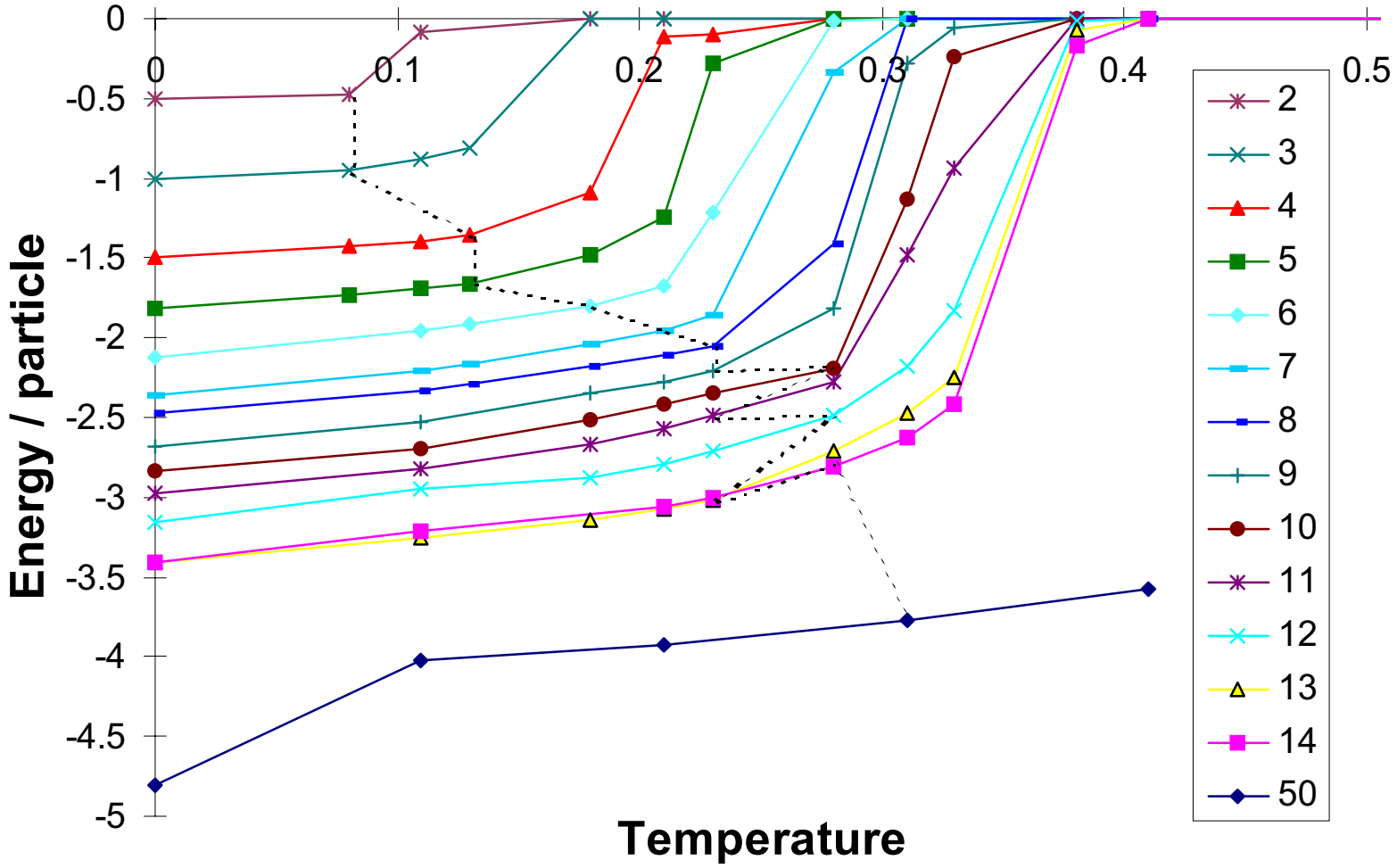
Cluster Size Distribution at End of Simulation



Initial cluster: 4 particles 11 particles 14 particles

- **Explanation**: smaller clusters have smaller binding energies and lower boiling points, so the dissociation of a particle may lower the boiling point sufficiently for quicker dissociation

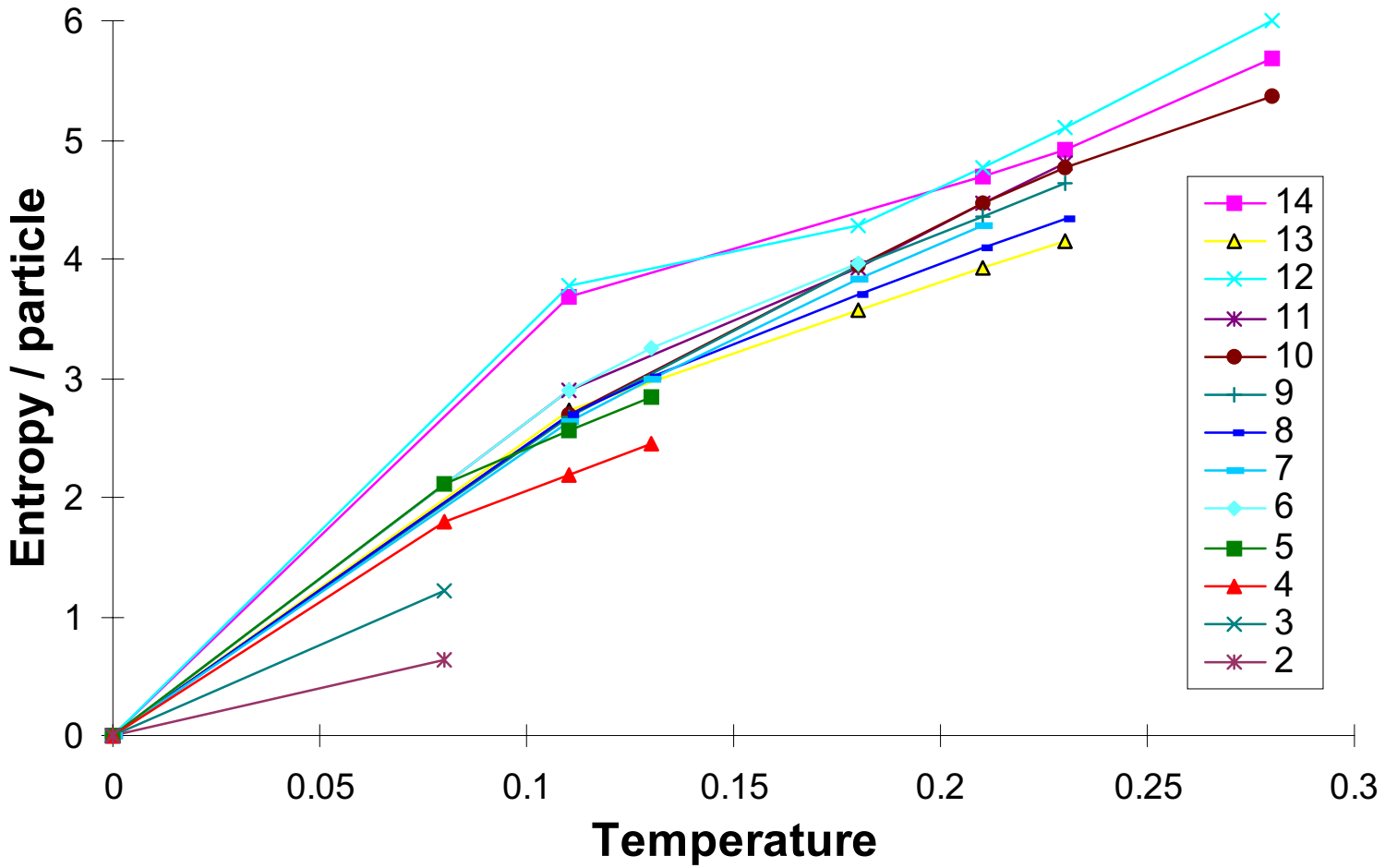
Potential Energy of Clusters



Dotted line is the boiling point: only intact clusters on and left of it.

Boiling point increases with N and with binding energy.

Entropy of Clusters

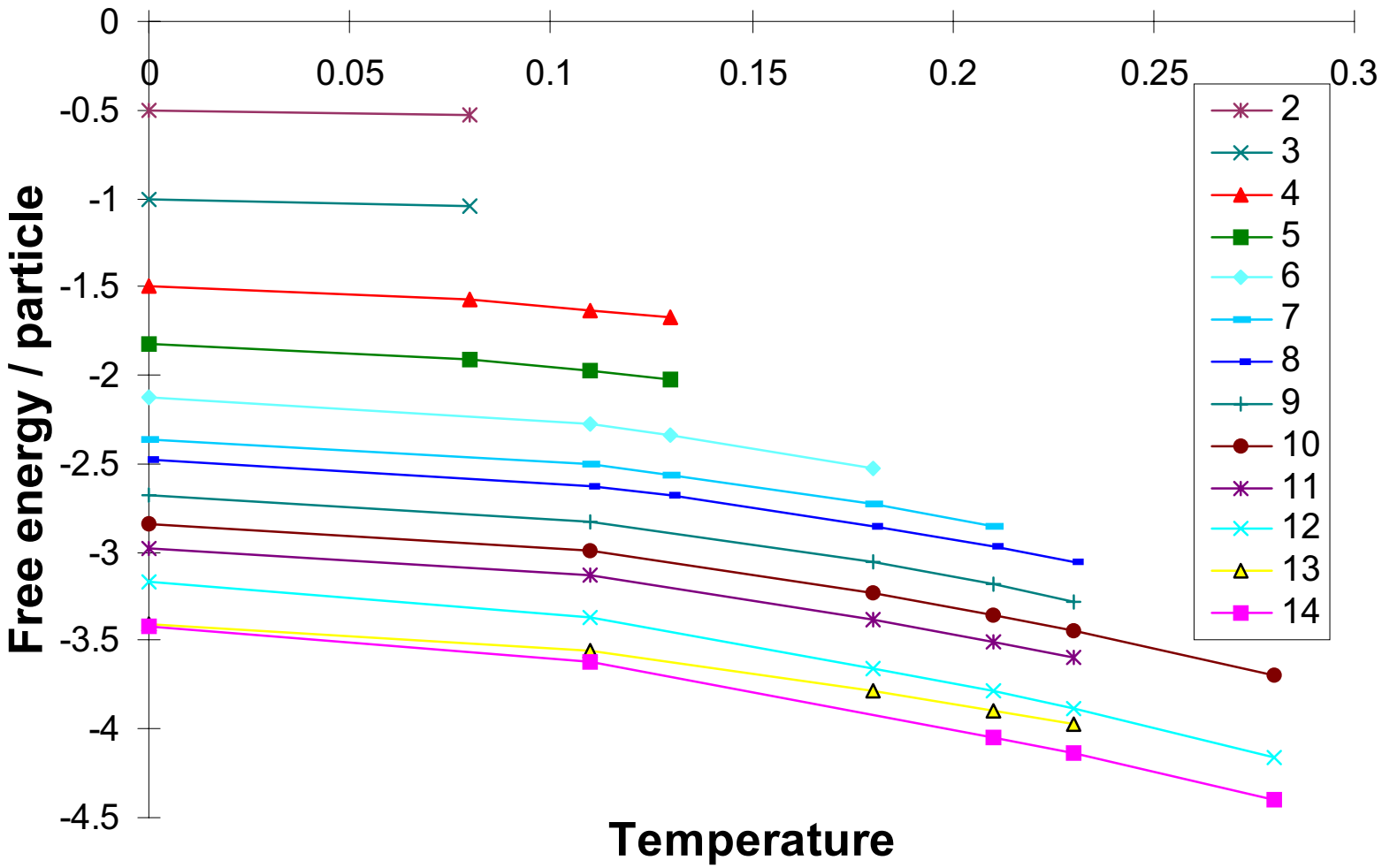


Calculated from $E(T)$ using $S(T) = \int_0^T \frac{1}{T} \frac{\partial E}{\partial T} dT$

Curves end at the boiling point

Bigger clusters have more entropy per particle

Free Energy of Clusters

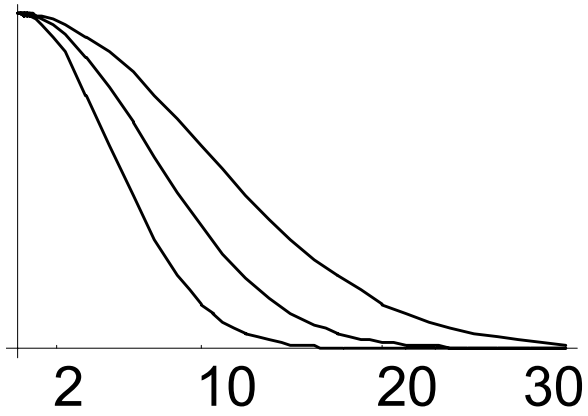


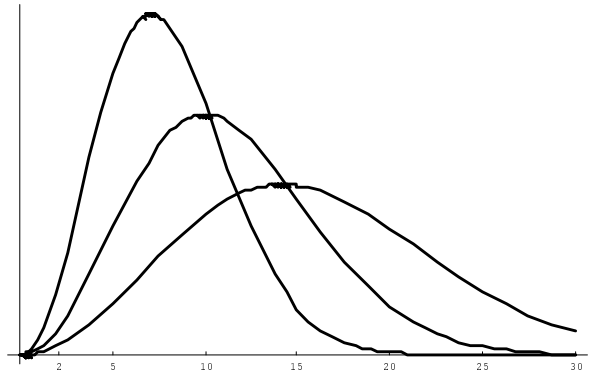
Calculated from $F = E\text{-}TS$
Curves end at the boiling point

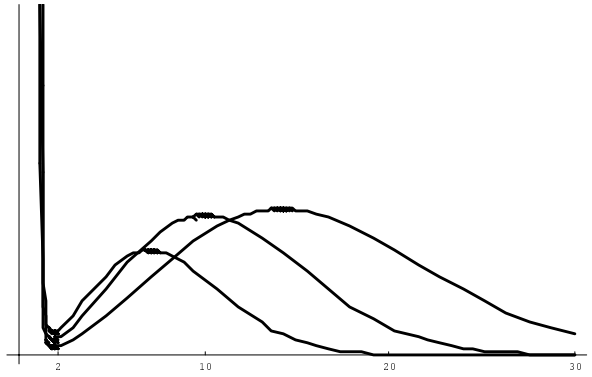
Model of a Two-Particle Cluster

- Model Monte Carlo simulation of a two-particle cluster as a random walk with transition probabilities from the Metropolis algorithm. Shown below are graphs of the probability that:

An unconstrained random walk:		Metropolis random walk with -1/r^6 potential:
Ends at a particular point at radius r:	Ends at any point at radius r:	Ends at any point at radius r:
$e^{-r^2/2\sigma^2}$	$r^2 e^{-r^2/2\sigma^2}$	$r^2 e^{-r^2/2\sigma^2+1/(kTr^6)}$

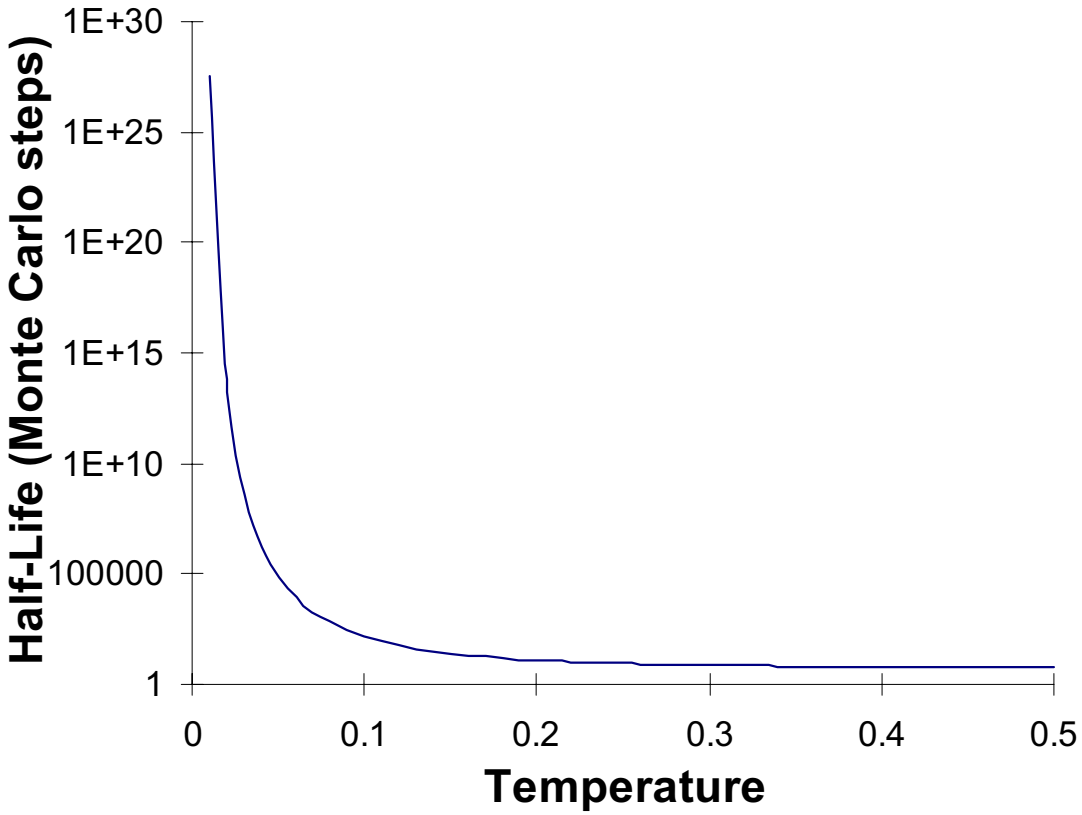






where $\sigma^2 = N/d$, *N* is the number of steps, *d* the number of dimensions
Above graphs have *T*=0.1, *N*=75, 150, and 300.

Model of a Two-Particle Cluster



Boiling point varies with the time scale, but very slowly.