Exercise 7: Grand-canonical Monte Carlo simulations near the critical point

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1 Results

1.1 Dependence with μ^*

In the following plots we can see a histogram showing how many times the system has been found with an specific number of particles, what we will call $h(N)$. Since the number of particles is not an intensive property, instead of showing N directly, we will divide by the volume in reduced units to find the density, which is indeed an intensive property.

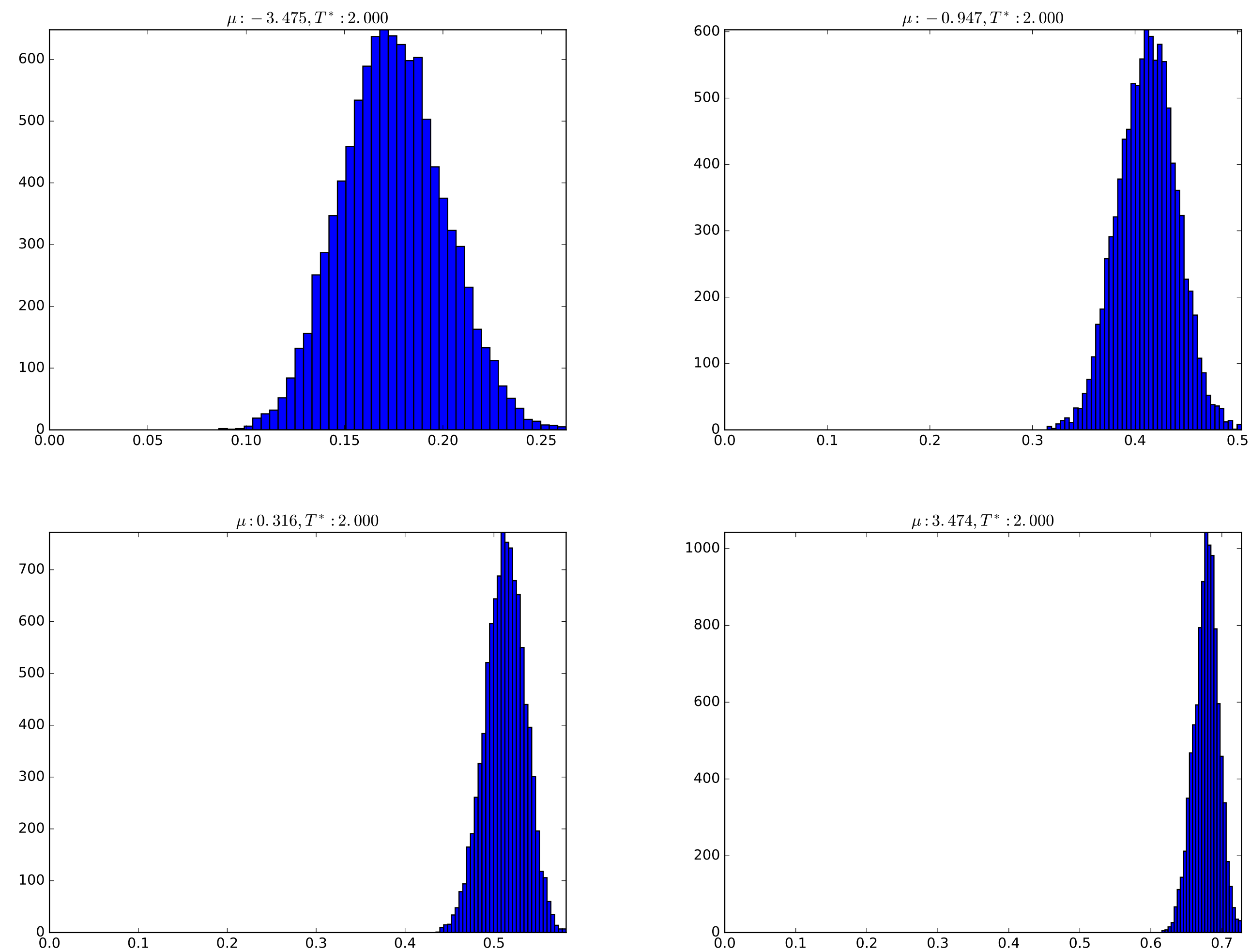

Figure 1: Several histograms $h(\rho)$ for different values of μ.

As expected, for lower values of μ^* the average density decreases, and increases for higher values. In the next section we will see a visual representation of this by looking at the equation of state $\mu - \rho$, and it will be clear how this value changes with μ.

1.2 Equation of state

From simulations in the NVT ensemble we can expect certain values of μ as a function of the density, that we can compare in the following plot:

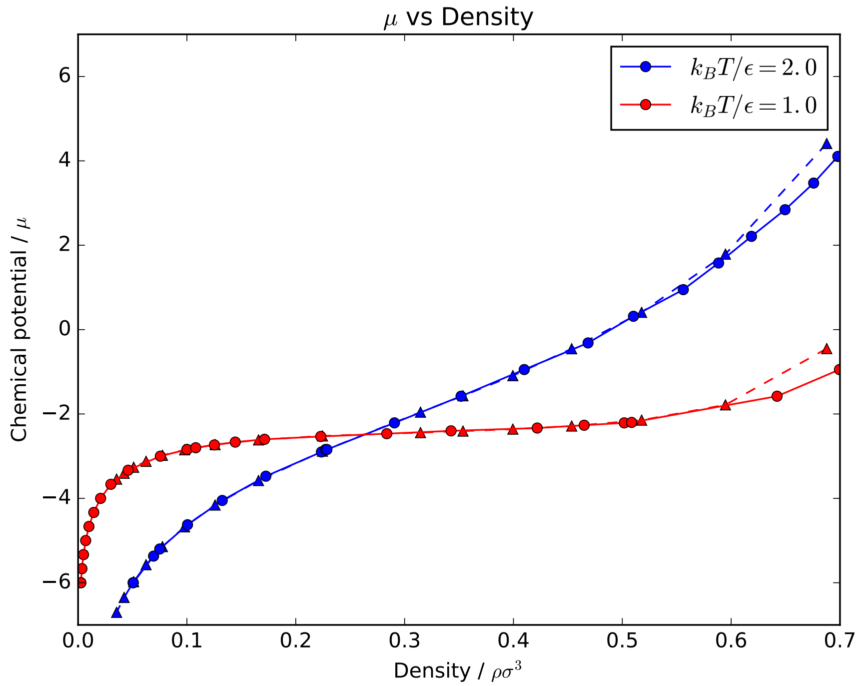

Figure 2: Plot of the equation of state, where the dashed lines with triangles are the results from the NVT simulation.

As we can see, there is a remarkable agreement at low densities, and increasingly less for $\rho \sim 0.6$ and larger, possibly because we need either more steps in the simulation as the system has not equilibrated yet (in this case we have started from an initial configuration at low density) or we need more particles in the system.

Moreover, from this plot we can easily see the region where the critical point is located, so our search in the next section will be tightly bounded.

1.3 Coexistence in the critical point

As we can see in the following histograms, we have found several values of (μ^*, T^*) for which the system is in a liquid phase at the same time as a gas phase.

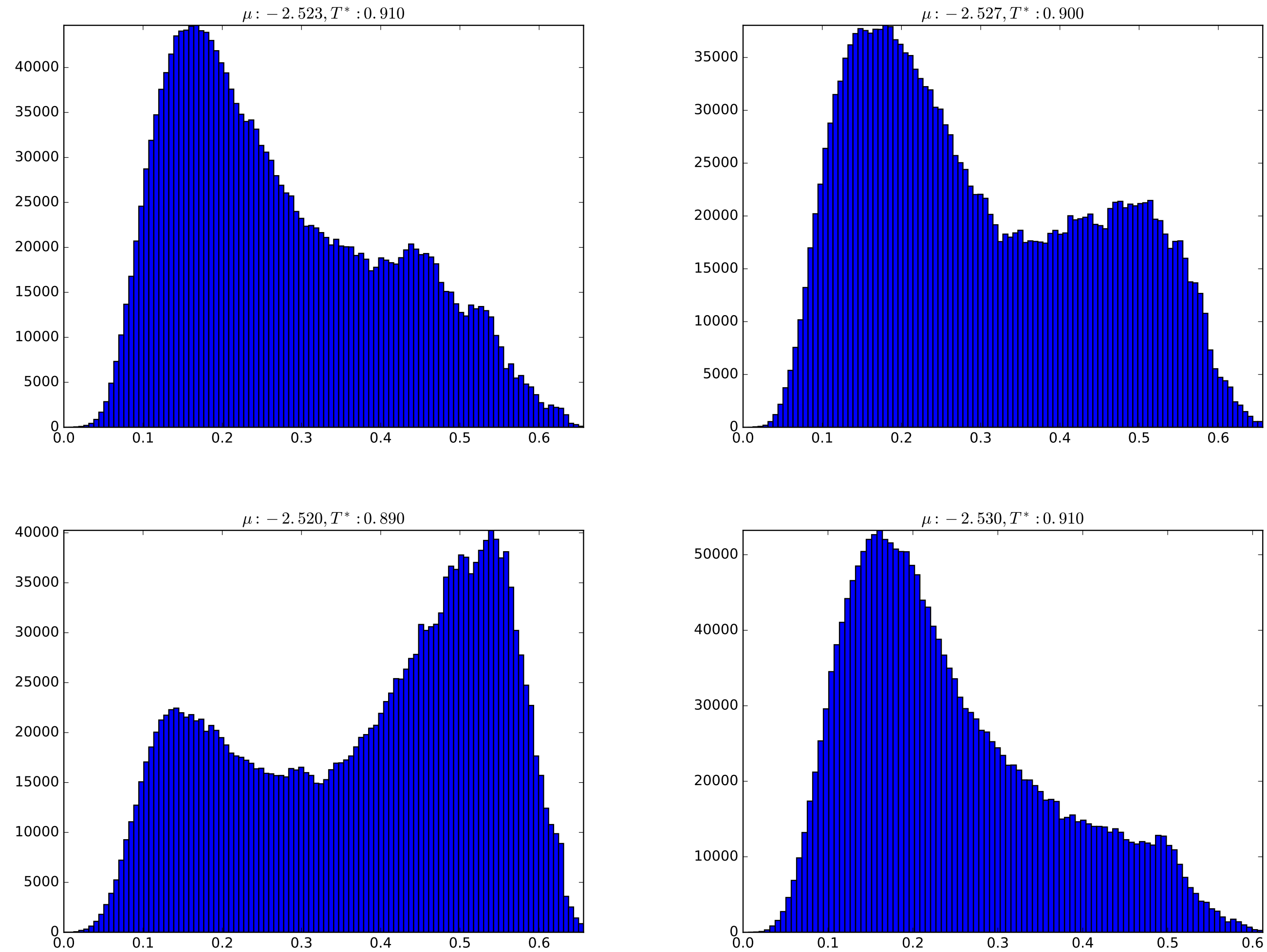

Figure 3: Several histograms $h(\rho)$ for different values of μ^* and T^*, showing coexistence.

By performing several simulations with different values of μ^* it is possible to find one for which the height of the peaks is approximately the same:

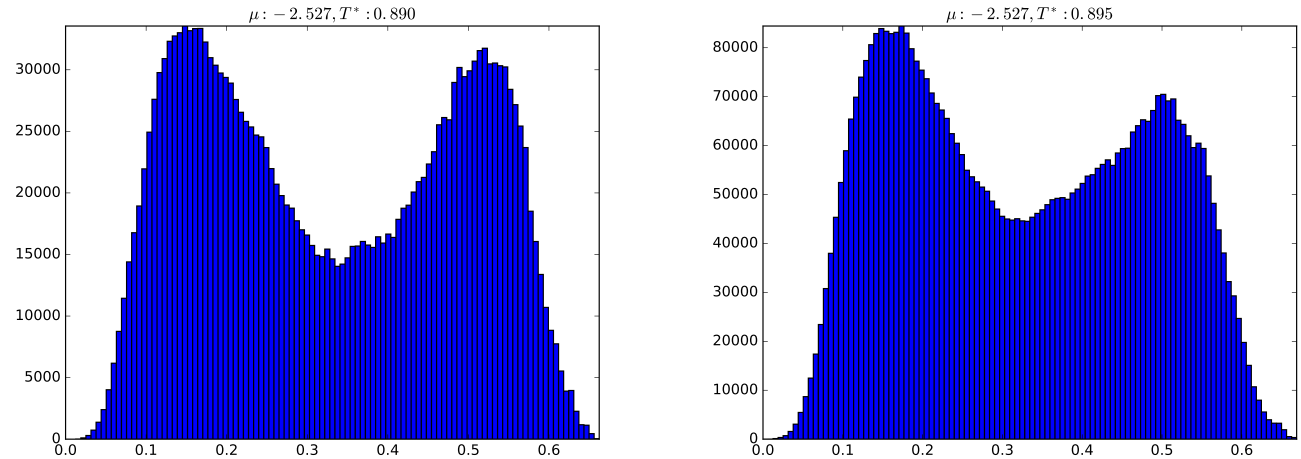

Figure 4: Histogram showing same-height peaks.

Plotting now these simulation's results in the $\rho - T^*$ plane we can see the following:

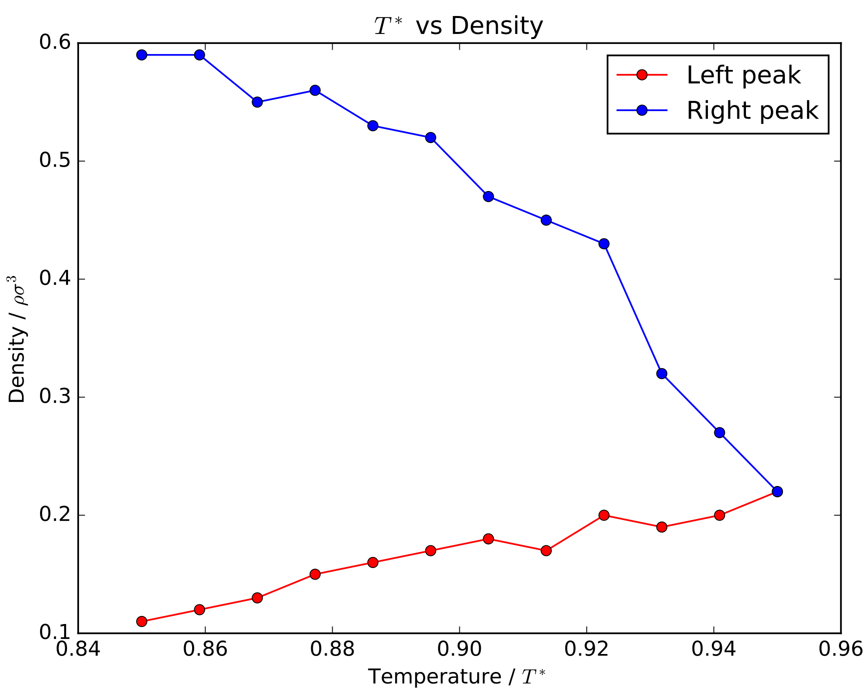

Figure 5: Histogram showing same-height peaks.

Here we can see a more-or-less linear relation for $\rho(T^*)$, which if we consider that the right peak is not completely resolved because we start with a low density configuration, a linear behavior is well inside the error bars.

Finally, $h(N)$ can be physically interpreted as the distribution density function of the particle number in the system, and can be related to the free energy if we consider that this energy is related to the derivative of the chemical potential with respect to the number of particles.

On the other hand, this method is clearly not going to work for low densities, as β in this case will be so high that any particle addition or subtraction will be unlikely to happen, and thus any simulation would take an unreasonable amount of time.

1.4 Representation

Finally we are going to visually compare two sets of snapshots of the system, simulated in the NVT ensemble with values of μ, T and ρ such that it's in the middle of two peaks.

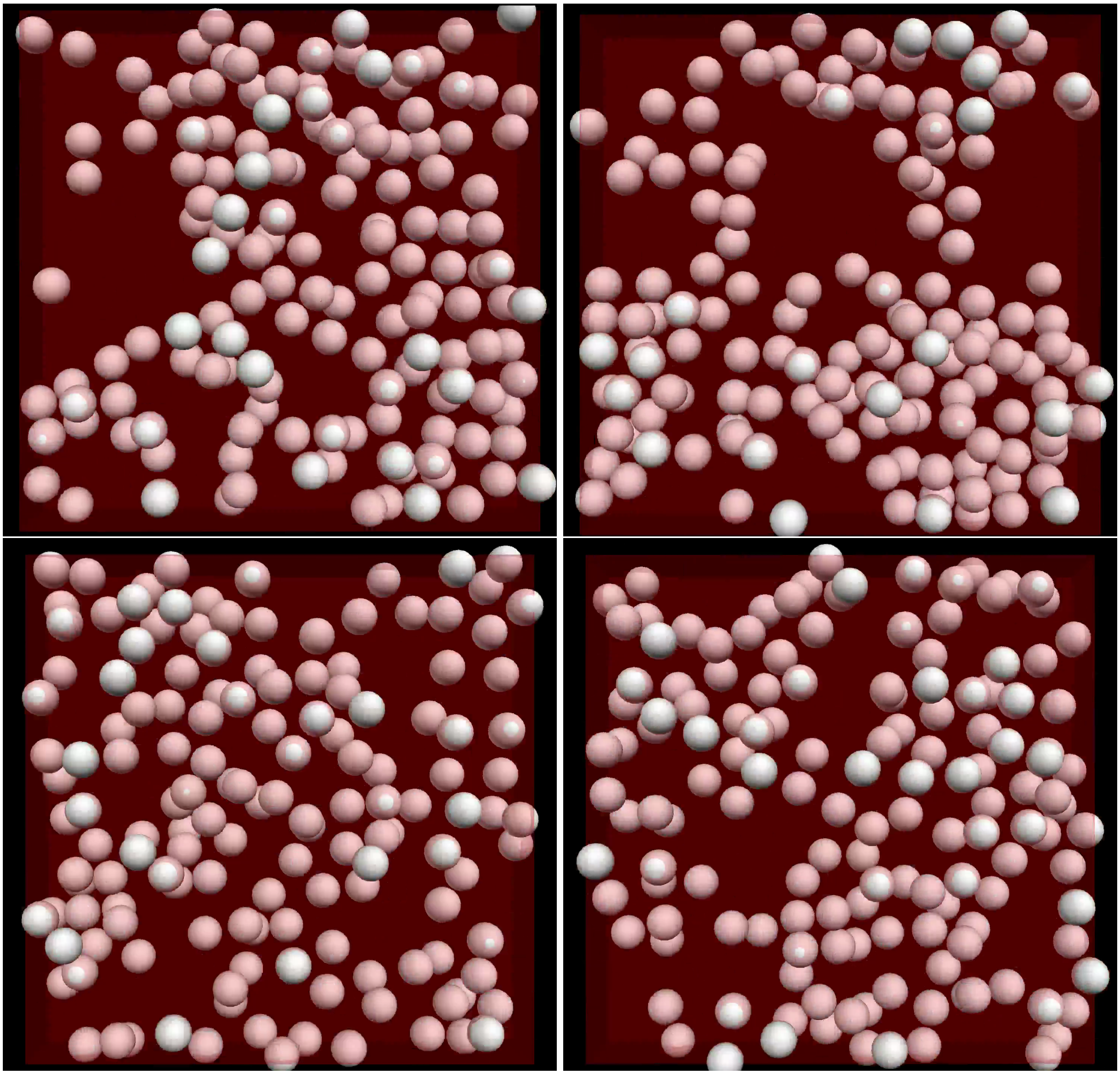

Figure 6: Several snapshots of the system, near the critical point (top) and far away from it (bottom).

We can notice that near the critical point there are regions with high density, in liquid phase, and others with way less particles, in the gas phase. On the other hand, when we get far away from it, in this case increasing the chemical potential, we cannot recognize this behavior any more as we could have expected.

Since the interfacial tension keeps particles together, when the system is close to the critical point it should increase, so particles in the liquid phase can be together.