Exercise 11

Homogeneous nucleation of argon
Nucleation is the first step in first order phase transition. Classic example is the gas-to-liquid conversion. Basically, this process is a continuous battle between the appearance and disappearance of small clusters, eventually producing clusters stable enough to grow further (see e.g. Vehkamäki, 2006 for more).

Nucleation is thus genuinely dynamical phenomenon and in this exercise you'll get to study it via molecular dynamics simulations. In general, this is not trivial. One needs to run long simulations and a fair amount of those. Luckily, the Lennard-Jones potential is able to produce nucleation events; so let's study LJ argon.

For the sake of an argument, let's choose the following conditions (in which nucleation should occur):

$$\rho^* = 0.0220 \text{ and } T^* = 0.662,$$

where the reduced density and temperature are $\rho^* = \rho\sigma^3 = \frac{N}{V}\sigma^3$, and $T^* = Tk_B/\epsilon$, respectively. The σ and ϵ are the Lennard-Jones parameters you are already quite familiar with. You can study a system as small as 500 atoms to run the simulations as fast as possible. Feel free to use a time step of 6 fs. Also, the Berendsen thermostat should perform adequately for the dynamics of nucleation.

Perform a decent number (≥ 50) of nucleation simulations (of several *nanoseconds*) and determine the size of the critical cluster, N^*, and the appearance rate of these clusters, that is, the nucleation rate J. Express J [(1/(volume × time)] in dimensionless reduced units, J^*. As usual, in addition to clear and detailed explanations, illustrate your investigations by nice graphs. Show also some representative pictures of the system in different stages of the nucleation process.

You are free to use any method you wish to perform the analysis. One possible way to proceed is the so-called mean first-passage time (MFPT) approach (Wedekind et al., 2007). Here one thinks of nucleation as an activa-

tion process: there is a potential energy barrier to be surmounted. The rate at which the barrier is crossed is the nucleation rate and the cluster at the top of the barrier is the critical cluster. For such a process the MFPT $\tau(N_0; a, b)$ is defined as the average elapsed time until the system starting out at some cluster size N_0 leaves a prescribed domain (a,b) for the first time. In this case τ can be given as

$$\tau(N) = \frac{\tau_J}{2} \left(1 + \mathrm{erf}[c(N - N^*)] \right),$$

where τ_J and c are parameters, erf[x] is the error function, N^* is the critical cluster size and the nucleation rate can be obtained as $\propto 1/2\tau(N^*)$ or as $\propto 1/\tau_J$. In practice, one needs to run simulations, record the first appearance times τ of all the (relevant) cluster sizes N from each simulation run, and to take an average of these. This yields a set of values $(N, \tau(N))$. By fitting the given equation to this data, one then obtains N^* and J.

Some practical considerations:

- you'll start with a box of gas with PBC – "a bulk gas", however, during the simulations your gas-phase system clusters quite heavily: in the end you'll have an infinite amount of large clusters in very diluted gas... comment about this, what it means both simulationally and physically

- you'll produce a lot of data – make sure that in your running scripts you delete the unnecessary files (or even better, do not print out those in the first place!)

- you can use the so-called Stillinger cluster definition: atoms belong to a cluster if they are within a radius of 1.5σ

- you might find the GROMACS function g_clustsize quite handy!

- it takes some human and computer time to run and analyse the simulations – start now!

Please return your solutions into the box in the second floor lobby by Thursday afternoon (28NOV2013) if you want some feedback. Alternatively, you can return your solutions at the exercise session on Friday (29NOV2013), starting at 11:15. This is the last session during this course.

References

Jan Wedekind, Reinhard Strey, and David Reguera, *Journal of Chemical Physics*, **126**, 134103 (2007).

Hanna Vehkamäki, *Classical Nucleation Theory in Multicomponent Systems*, Springer 2006.