

Laboratory of Computational Physics

BY LUCA CASSIA

Dipartimento di Fisica, Università di Milano-Bicocca
I-20126 Milano, Italy

Email: l.cassia@campus.unimib.it

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1 Hard-Core Molecular Dynamics in 3d

In this section we repeat the study of molecular dynamics with hard-core central potential for 3d systems. As for the 2-dimensional case, we work with identical particles enclosed in a box with PBCs and use adimensional units of length, time and mass:

$$L = 1, \quad m = 1, \quad k_b T = 1 \quad (1)$$

1.1 Thermalization

The system is initialized in a BCC lattice (Fig.1). This type of sphere packing has a packing density:

$$\eta = \frac{N\pi\sigma^3}{6L^3}, \quad \sigma = \sqrt[3]{\frac{6\eta}{\pi N}} L \quad (2)$$

which takes its maximum value for $\sigma^3 = (3\sqrt{3}L^3)/4N$:

$$\eta_{\max} = \frac{\pi\sqrt{3}}{8} \approx 0.68017476158... \quad (3)$$

The momenta of the particles are initialized with uniform distribution inside the range $[-1, 1]$ with total momentum equal to zero (center of mass reference frame). After the initialization the momenta are rescaled in order to obtain the desired temperature. As before, we have the relation between kinetic energy and temperature:

$$K = \frac{d}{2} N k_b T, \quad T = \frac{2}{d N k_b} K \quad (4)$$

We now study the mixing properties of this type of system. We evolve a system of $N = 100$ particles from its initial configuration, for 10^4 collisions and measure the pressure (Fig.1) and the mean free path (Fig.2) every 10 collisions. This procedure is also repeated for $N = 400$.

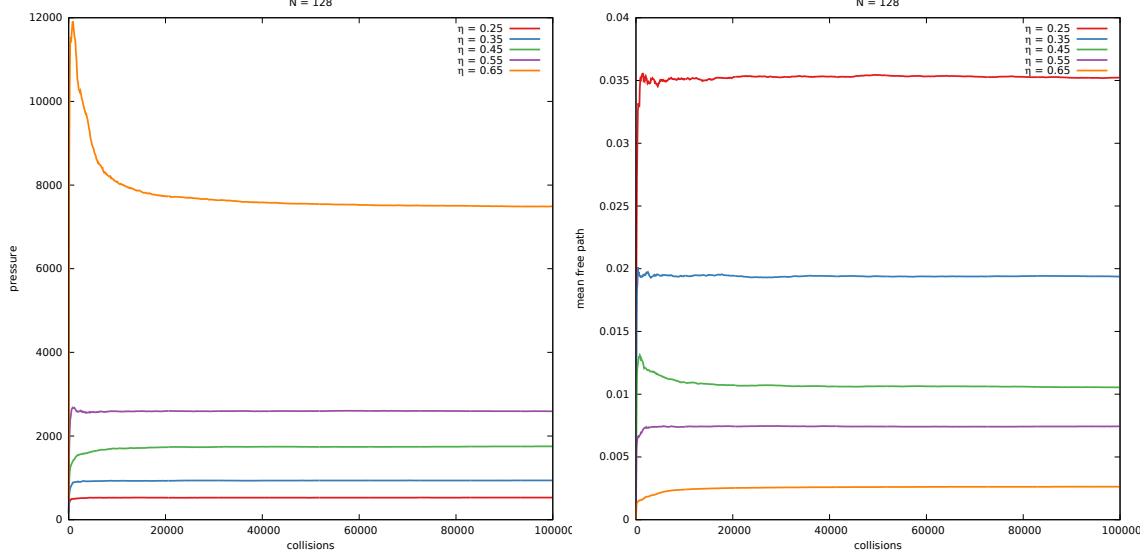


Figure 1. Plot of the thermalization process of an hard-core interacting gas of $N = 128$ particles. On the left is the pressure as a function of the number of collisions, while on the right is the mean free path of the particles. Different colors represent the different values of $\eta = 0.25, 0.35, 0.45, 0.55, 0.65$ used for the simulations.

We consider the system thermalized after $5 \cdot 10^4$ collisions where we expect a momentum distribution of the Maxwell-Boltzmann type. The distribution obtained from the simulation confirms our choice of thermalization time:

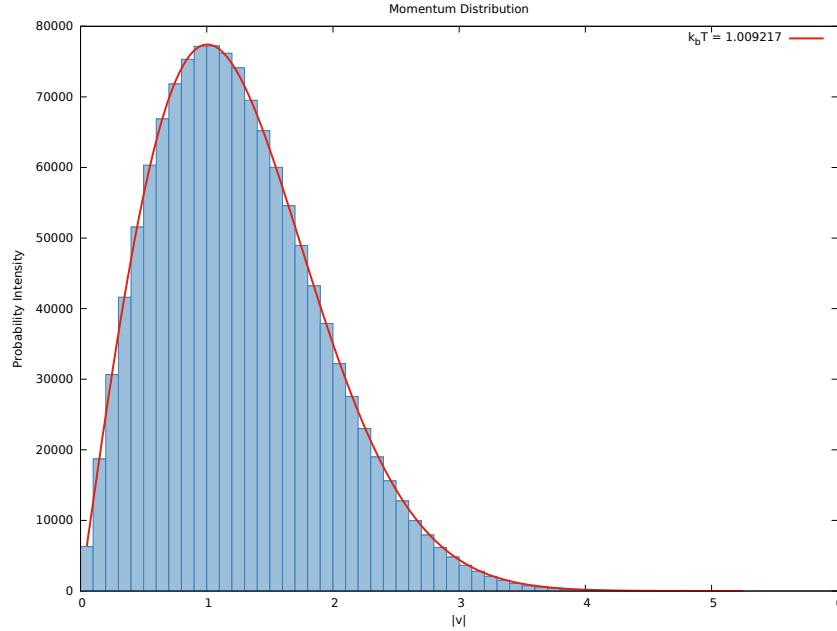


Figure 2. Histogram of the modulus of the momenta for $N = 128$ particles at $\eta = 0.5$. The measurements are taken after $5 \cdot 10^4$ collisions from the start of the simulation, and after that every 500 collisions for a total of 10^4 datasets each containing the momenta of N particles.

By fitting the histogram we obtain the result:

$$k_b T = 1.00922 \pm 0.00559 \quad (5)$$

which is remarkably close to the numerical value $k_b T = 1$ that was set at the beginning of the simulation.

1.2 Phase Transition

In this section we study the η dependence of the pressure P for a system of $N = 250$ particles. As for the 2-dimensional case we use the formula:

$$\frac{PV}{N k_b T} = 1 + \frac{1}{2Kt} \sum_{c=1}^{N_c} m \sigma |\Delta \vec{v}_{ij}(t_c)| \quad (6)$$

Again the measurements are taken by averaging over independent simulation runs in order to reduce autocorrelation effects. Every point of in (Fig.3) is the mean value of 10 independent simulation thermalized for a time corresponding to $5 \cdot 10^4$ collisions.

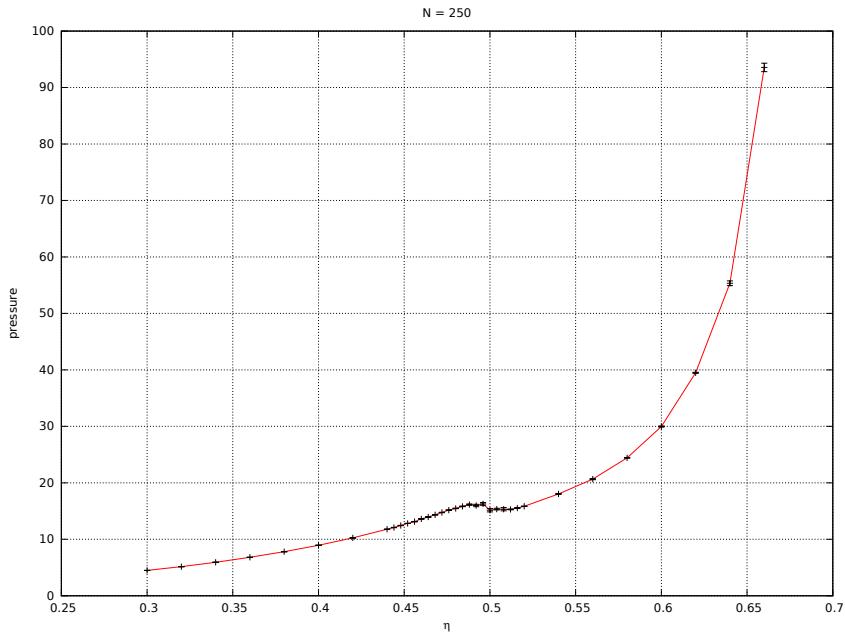


Figure 3. Plot of $\frac{PV}{Nk_b T} - 1$ as a function of η for a system of 250 particles. Every measurement is taken from the average of 10 independent runs each collected after an initial thermalization time of $5 \cdot 10^4$ collisions. The errorbars represent the standard errors of the averages.

For the 3 dimensional case at study, we notice a discontinuity of the pressure around the value $\eta \sim 0.5$. Near the transition point the measurements are averaged over the two metastable branches of the curve, thus forming almost a plateau, which is a typical property of first order phase transitions.

1.3 Mean Squared Displacement

Informations about the phase of the system and about its diffusive/confined properties are also found by looking at the mean squared displacement:

$$\text{MSD} = \langle (\vec{r}_i(t) - \vec{r}_i(t_0))^2 \rangle = \langle \Delta \vec{r}(t, t_0)^2 \rangle \quad (7)$$

which, for a 3 dimensional system enclosed in a box with edge $L=1$, has a plateau at:

$$\lim_{\Delta t \rightarrow \infty} \text{MSD}_{3d} = \frac{L^2}{4} = 0.25 \quad (8)$$

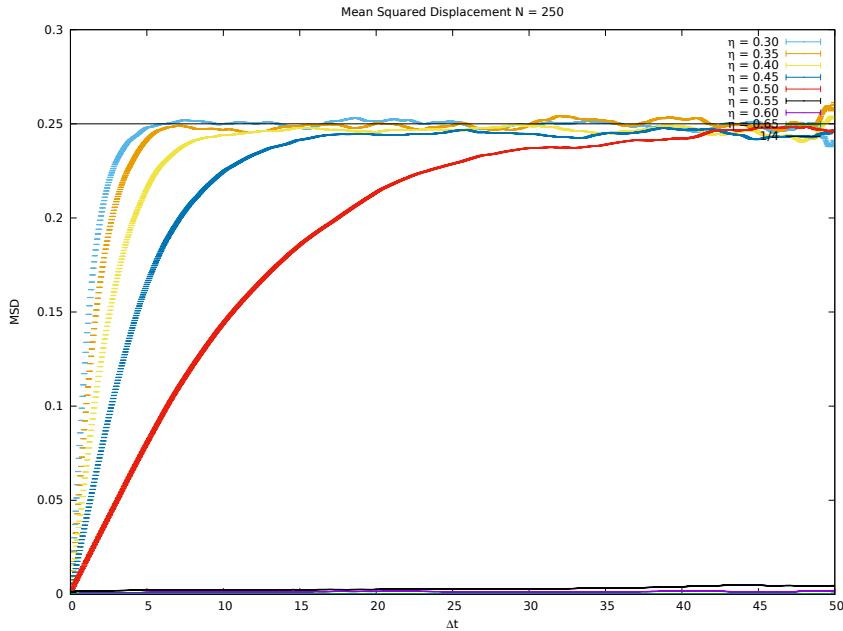


Figure 4. Mean squared displacement from a simulation of $N = 250$ particles. The measurements are taken for a simulation time $t_S = 50$ with a time step of 0.005 after a thermalization of $5 \cdot 10^4$ collisions. The color palette represents different values of η . The solid line in black is the exact result for $\Delta t \rightarrow \infty$.

From the growth of the MSD with time, we note a similar behavior to that of the 2 dimensional case. This time, though, the discontinuity in the rate of change of the coefficient D with respect to η is even more drastic. For $\eta < 0.5$ the particles have an initial diffusive dynamics that becomes

confined when the plateau value 0.25 is reached. Immediately after $\eta \sim 0.5$ the diffusion coefficient drops almost to zero and we witness a transition to a solid phase of the system where the particles are strongly confined by the small space available.

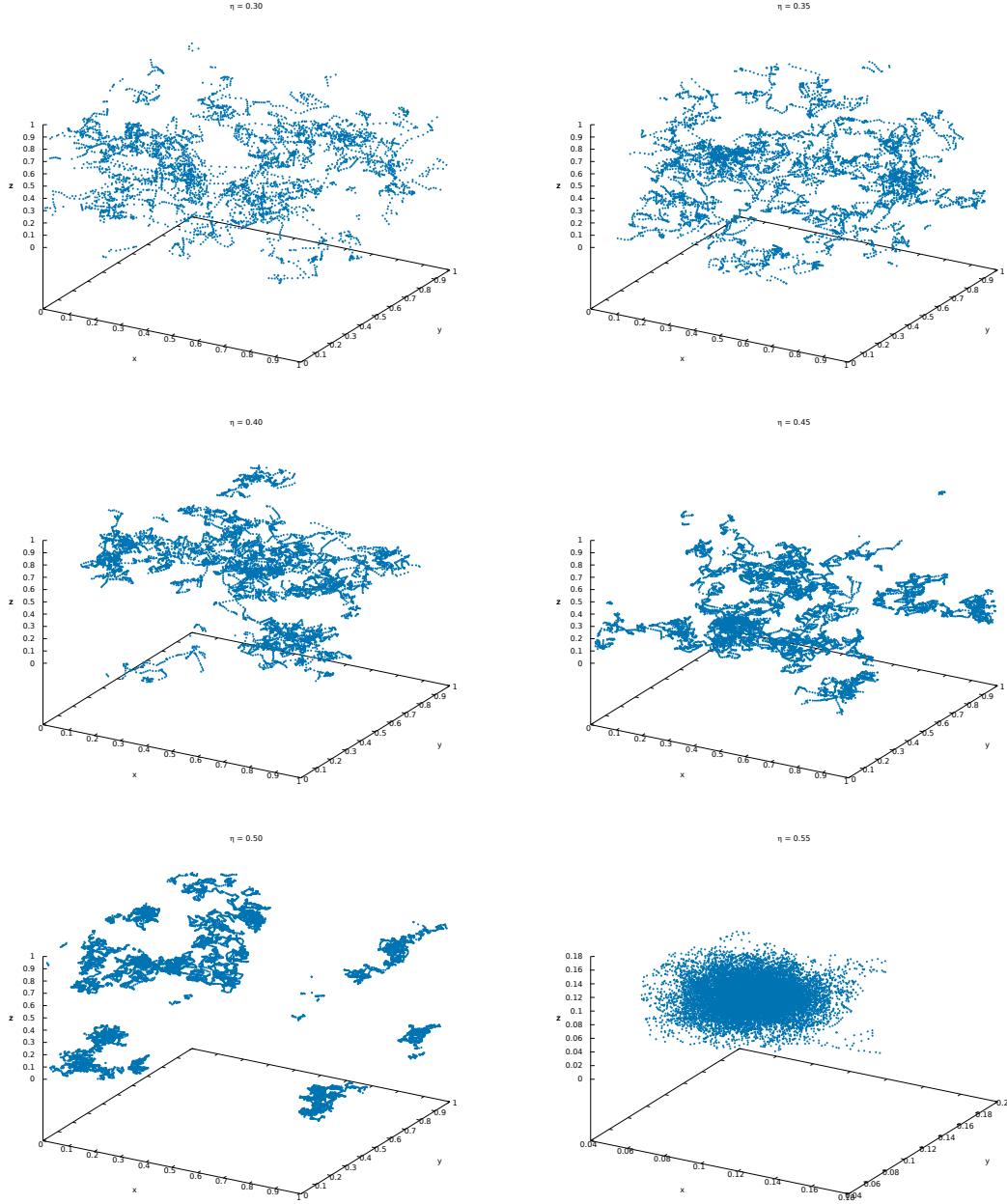


Figure 5. Points visited by individual particles in a system of $N = 250$ total particles, at different values of the packing density η . The first five picture represent the typical trajectories of diffusion processes such as random walks (liquid phase). In the last picture is evident the confining property of the solid phase of the system.

1.4 Thermodynamic Limit

Finally we study the thermodynamic limit of the pressure by taking several measurements at

growing values of V and N keeping the density η fixed (instead of actually scaling the volume V we increase the number of particles and reduce their diameter so that $\eta = \text{const}$).

We consider systems with $N = 32, 64, 128, 256, 512$ and measure the quantity:

$$\frac{PV}{Nk_bT} - 1 = \frac{m\sigma}{2Kt} \sum |\Delta \vec{v}_{ij}| \quad (9)$$

at the fixed value $\eta = 0.3$. We then plot the results against $1/L$ and perform a linear fit of the form:

$$y = p_0 + p_1 x \quad (10)$$

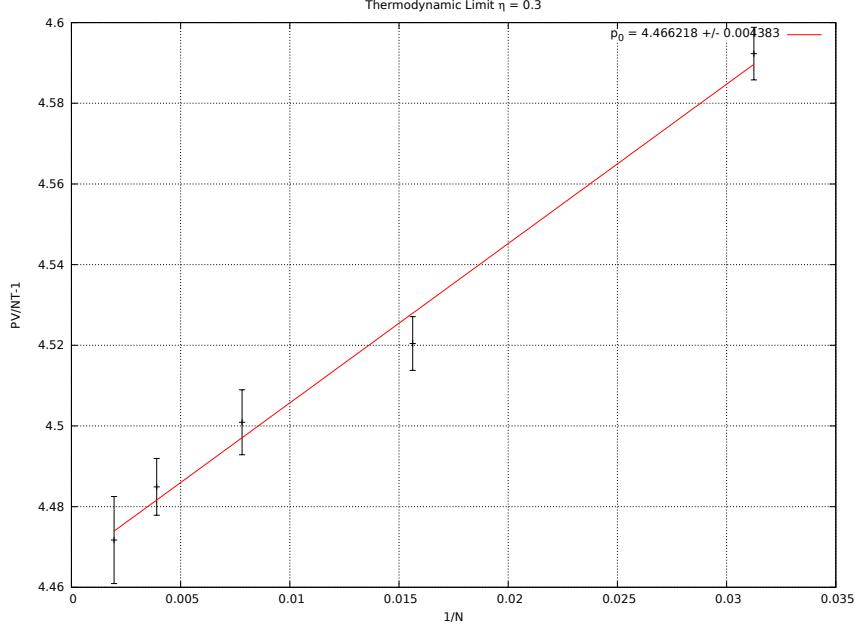


Figure 6. Plot of $\frac{PV}{Nk_bT} - 1$ as a function of $1/L$. Each point is taken after thermalization and averaged over 10 independent simulation runs. The errors are computed as the standard error on the mean values.

The result of the fit indicates that:

$$\lim_{N \rightarrow \infty} \frac{PV}{Nk_bT} - 1 = 4.4662 \pm 0.0044 \quad (11)$$