Dynamics of heterogeneous crystallization of parallel hard squares: A dynamic density functional theory study

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We used the Dynamic Density Functional Theory [1] to study the relaxation dynamics of confined parallel hard squares from initial conditions different from the final equilibrium profiles (having a crystalline (K) symmetry). The confinement is implemented through a soft repulsive periodic external potential resulting in a collection of cavities separated from each other by repulsive barriers. The Density Functional used was that based on the Fundamental Measure Theory [2]. We characterized the dynamics of the sequential growth of crystalline layers inside the cavities through different magnitudes: (i) the interlayer and intra-layer fluxes of particles, (ii) the characteristic time to reach the equilibrium, (iii) the nonlinearities of fluxes measured through the numbers of their extrema as a function of time, and (iv) the heights of the density peaks. In general when the dimensions of cavities favor the formation of well defined crystalline layers with sharp peaks the dynamics is faster and strongly nonlinear with intra-layer fluxes being dominant with respect to the interlayer ones. The opposite occurs when the dimensions of cavities disfavor the formation of a crystalline phase: the fluxes are monotonic with the interlayer ones being the dominant while the time to reach the equilibrium is dramatically raised.

In a second study we applied the same theoretical tool to study the heterogeneous nucleation of non-uniform phases such as the columnar (C) or the K phases. The growth of C and K phases are induced by the presence of objects, with circular, square-like, rectangular and triangular geometries and of different dimensions. We found that except for the rectangular object with large aspect ratio the K phase has a higher propensity to nucleate while the more stable phase at bulk is the C. In Fig. 1 we show a sequence of density profiles taken at different times of the dynamic evolution of K (a) and C (b) nucleation around a circular (a) and rectangular (b) geometries.
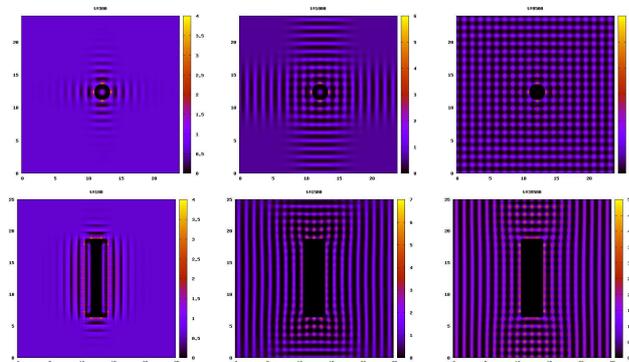

Figure 1: A sequence of three evolving density profiles corresponding to heterogeneous nucleation of parallel hard squares from a circular (top) and rectangular (bottom) objects.

[1] U. M. B. Marconi and P. Tarazona, J. Chem. Phys. **110**, 8032 (1999).

[2] J. A. Cuesta and Y. Martínez-Ratón, J. Chem. Phys. **107**, 6379 (1997).