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Propagation of solid-liquid interfaces under disordered confinements

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Recent progress in the synthesis of nanoporous materials with controlled structural properties made it possible to address various phenomena occurring in mesoscalic systems. Among them, different aspects of fluid phase transitions can now be related to the structural properties of the mesoporous matrices. In this work, we present the results of our experimental studies of crystal growth processes in mesoporous silicon, which was fabricated to have linear, macroscopically long pores. Notably, in an ideal cylindrical pore one expects a reduction of the freezing temperature in proportion to the pore size. In the material under study, however, freezing is found to start already before the transition temperature, determined by the average pore size, is reached. The kinetics of this process is found to be very slow and to depend on the temperature. In particular, power-law dependencies of the ice phase invasion into the pores were observed. These findings we have associated with the fact that the material under study possesses a substantial degree of disorder, namely there exist a distribution of the pore diameters along the pore axis. In light of this, the results obtained have been discussed assuming that the crystal growth processes under such strong confinements is an activated process, requiring overcoming of the pore size-dependent barriers in the free energy, rendering the overall process to occur under the occurrence of the disordered transition rates.

To justify the macroscopic model for the ice invasion kinetics, we have developed a simple lattice-fluid model [2], which is capable to model the freezing and melting processes of fluids confined to pores with arbitrary organizations of their pore spaces. We demonstrate that this microscopic lattice model reproduces quantitatively most experimental observations obtained using porous materials with very different pore geometries. As an important point, this model shows the occurrence of the confinement size- and temperature-dependent ice phase propagation rates. This finding, thus, validates the use of the macroscopic model with distribution of the free energy barriers along the pore axis, which may be considered as a coarse-grained version of the microscopic one. Different regimes of the ice phase propagation, including, in particular, the observation of Sinai-like diffusion, will be discussed [3].

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References

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