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Propagation of Solid-Liquid Interfaces in Disordered Linear Pores

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1. Introduction

Recent progress in the synthesis of nanoporous materials with controlled structural properties made it possible to address various phenomena occurring in mesoscalic molecular systems. Among them, different aspects of fluid phase transitions could now be related to the structural properties of mesoporous matrices. In particular, porous materials with well-defined pore geometries and pore sizes, such as MCM-41 or SBA-15, have been successively used to verify theoretical predictions about confinement-induced shifts of the transition points [1]. In this work, we take advantage of the option to prepare mesoporous silicon with linear, tailor-made pores [2] and thus to study the dynamics of the freezing process of a fluid under well-defined conditions of confinement. Most importantly, by having macroscopically-long linear, isolated pores, all relevant phenomena can be studied free of network effects, which may enormously complicate the data analysis.

2. Experiment

In the present work, we have experimentally studied the kinetics of the freezing of nitrobenzene confined to pores of mesoporous silicon by means of nuclear magnetic resonance (NMR). Mesoporous silicon has been carefully prepared to consist of tubular pores, isolated from each other, with a pore diameter of about 6 nm [3].

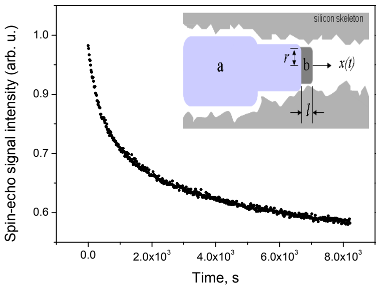

Fig.1: Typical evolution of the spin-echo signal intensity measured in a sample of mesoporous silicon saturated with nitrobenzene upon a stepwise change of temperature (cooling branch). The inset shows a cartoon-like model of the freezing process in a disordered, linear pore.

Fig. 1 demonstrates a typical result of this study, by showing the NMR spin-echo signal intensity as a function of the observation time measured upon a stepwise decrease of temperature [4]. The NMR experiment has been designed in a way to yield measured signal being proportional to the volume occupied by the liquid phase in the pores. Thus, the signal reduction in Fig. 1 indicates the decrease of this volume due to progressing freezing of the pore fluid. The process of freezing is found to be very slow and can be, at long times, approximated by a power-law dependency t^a, with a temperature- and pore size-depend exponent $a < 1$.

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To explain such a behavior, we suggest a thermodynamical model taking account of mesoscalic disorder in porous silicon (see inset in Fig. 1). The latter inherently results from the preparation procedure. Due to this disorder, it may appear that freezing of a pore section (b), filled with the liquid and adjacent to the frozen part of the pore (a), may result in a reduction or in an increase of the overall free-energy of the system. Thus, under certain conditions, the solid front penetration may require activated overcoming of the barriers in the free energy.

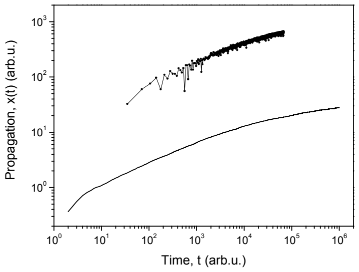

Fig.2: Solid-liquid interface position averaged over many pores obtained experimentally (symbols) and calculated (line).

Depending on temperature, average pore size and pore size distribution, which determine the magnitudes of the barrier heights and their distribution, the times required to freeze or melt the individual pore segments can be very broadly distributed. Hence, depending on temperature, the propagation of the solid-liquid interface in such a pore, which generally may be described by a trap-model with a random distribution of the transition rates, may exhibit a very reach behavior. We address this issue by means of Monte Carlo simulations based upon the suggested model. In this way, we find conditions under which we may satisfactorily reproduce our experimental data (Fig. 2). Thereafter, the model is used to explore other experimentally relevant regimes, where the interface propagation exhibits different patterns, such as Sinai diffusion.

3. Conclusions

In this work, we have experimentally studied the kinetics of freezing of fluids in linear pores using the NMR technique. The kinetics are found to exhibit a very complex behaviour depending on the experimental conditions. We suggest a thermodynamical model capturing the main features observed in the experiments. It takes account of the fact that the propagation of the solidification front into a pore having a certain degree of disorder may require overcoming temperature- and pore size-dependent barriers in the free energy.

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