Study of crystallization in confined system

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INTRODUCTION

There are many mysterious phenomena related to confined systems in nature. Confined system is the subject of intense interest. In particular, water confined in nanoscale geometries has garnered much recent attention because of its biological and technological importance [1,2]. Confinement lowers the melting temperature of ice[3],leading to many accomplishments in supercooled water. But now it is still not clear about nucleation process in confined system and which factors affect the crystallization in confined system. In this work we use molecular simulations with the smooth Jagla potential model to investigate the crystallization in confined systems.

MODELS AND METHODS

We perform molecular dynamics (MD) simulations of a system confined between two surfaces. Simulations are performed at NVT ensemble, particles are confined between two infinite surfaces, as shown schematically in Fig. 1. The particles interact via the smooth Jagla potential model, as shown in Fig.2. The interaction between particle and surface is Lennard-Jones 9-3.

$$u(r) = \frac{3\sqrt{3}}{2}\varepsilon\left[\left(\frac{\sigma}{r}\right)^9 - \left(\frac{\sigma}{r}\right)^3\right]$$

The interaction strength is ε, see Fig.3. Energies and distances are reported in units of ε_0 and a respectively. T=0.13, lower than the melting temperatures of all simulated systems.

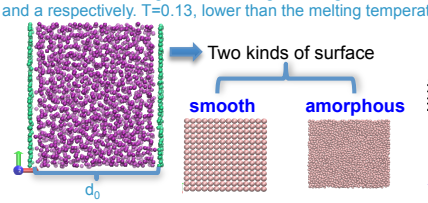

Fig.1. Sketch figure of the simulated system. Particles are confined between two surfaces in yz plane, Ly=20, Lz=20. Periodic boundary conditions are used in the y and z directions parallel to the surface .

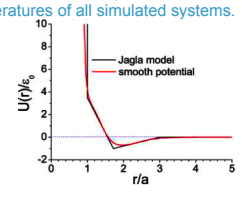

Fig.2. The smooth Jagla potential (red curve). The minimum is $-\varepsilon_0$. The effective hard-core distance is a.

The orientational order: $Q_l = \left[\frac{4\pi}{2l+1}\sum_{m=-l}^{m=l}|Y_{l,m}(\theta,\varphi)|^2\right]^{1/2}$

For *l*=6, Q_l has maximum value for most crystals such as hcp, fcc[4].

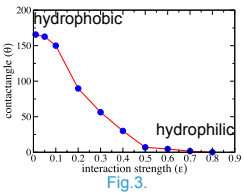

Fig.3.

RESULTS

A. Crystallization in confined systems within two surface structures

ε=0.1 (hydrophobic surface), d_0=15 (separation between two confined surfaces).

For smooth surface system :

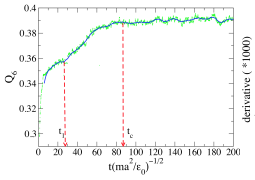

Fig.4. The orientational order in smooth surface system

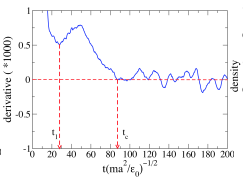

Fig.5. The derivative in smooth surface system

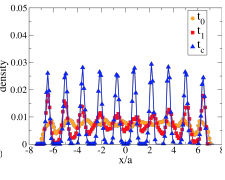

Fig.6. The density profile in x direction in smooth surface system

According to the changing of orientational order and density profile, we divide the crystallization process into two steps: **mainly ordering, ordering and layering.**

For amorphous surface system:

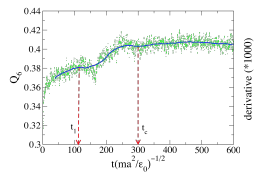

Fig.7. The orientational order in amorphous surface system

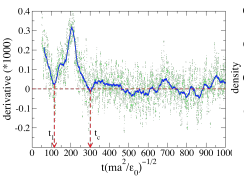

Fig.8. The derivative in amorphous surface system

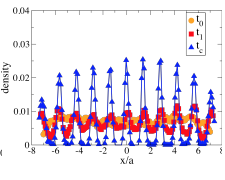

Fig.9. The density in x direction in amorphous surface system

For smooth surface system and amorphous system, the crystallization process in confined system involves two steps: mainly ordering, ordering and layering.

B. The effects of different surface structures on crystallization time

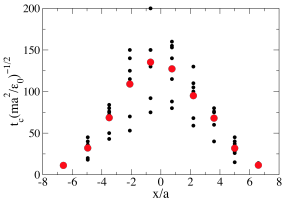

Fig.10. Each layer's crystallization time in smooth surface system. ε=0.1,d_0=15.

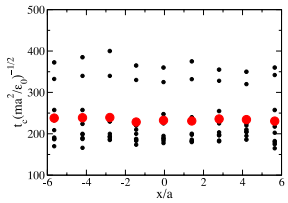

Fig.11. Each layer's crystallization time in amorphous surface system. ε=0.1, d_0=15.

For smooth surface system, layers finish crystallization one by one from surface to the middle. For amorphous surface system, layers finish crystallization almost homogenously.

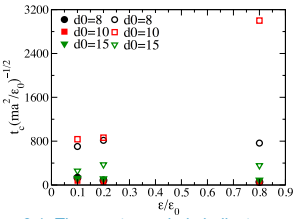

Fig.12, ε=0.1. The empty symbols indicate amorphous surface systems. The solid symbols indicate smooth surface systems.

For d_0=8, 10, 15, ε=0.1, 0.2, 0.8, smooth surface systems crystallize faster than amorphous surface systems.

C.The effects of interaction strength on crystallization time

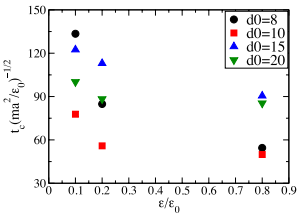

Fig.13. Crystallization times of smooth surface systems with different separations and interaction strengths

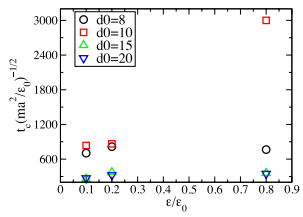

Fig.14. Crystallization times of amorphous surface systems with different separations and interaction strengths

The stronger the interaction is, the faster the crystallization is in smooth surface systems. While the effect of interaction strength is not apparent in amorphous surface system.

CONCLUSION

(1) Crystallization process involves two steps:

- ordering
- ordering and layering

(2) The surface structure effects

- Smooth surface: from two sides to the middle
  Amorphous surface: almost homogeneously
- Crystallization in smooth confined surface system is faster than amorphous walls system

(3) The effects of interaction strength between particle and surface

- For smooth surface, the effect of interaction strength is distinct,
  more hydrophilic surface, faster crystallization
- For amorphous surface, the effect of interaction strength is not apparent

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