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Master thesis proposal

Phase-field simulations of crystal anisotropy and sintering using a FEM-based framework

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1 Introduction

Many large scale industrial chemical production processes as well as environmental protection processes include the use of heterogeneous catalysts [6]. In heterogeneous catalysts used in gas/solid reactions, chemical species are adsorbed on a solid surface, on which reactants react and are consequently released in the surrounding phase. Since reaction rates and selectivities vary based on the different crystal facets, edges and corners [13], the knowledge of catalytic surface is necessary to model reaction kinetics efficiently.

Interfaces contribute to an excess in free energy due to a disruption of intermolecular bonds at the surfaces. Different orientation of interfaces, and so different molecular arrangements lead to a variation in this interfacial energy: a surface energy anisotropy. The different shapes of crystals can be understood as a constrained optimization of the surface energy in order to minimize their total free energy, with the size/number of atoms in the particle as the constraint. The equilibrium shape of crystals can thus be predicted with the knowledge of surface energy anisotropy, for example using the analytical Wulff -construction method.

Nevertheless heterogeneous catalyst are often operated under dynamic conditions like start and shut -down operations, variations in temperatures or variation in feeds, which may change the catalyst morphology. This changes may be caused by a temperature dependency of the catalytic interface [12], or by reactions of the catalyst surface with a chemical species in the gas (like an oxidation of the catalyst [17]) and consequentially change in the surface energy. To better understand the kinetics/catalyst interaction a time dependent evolution analysis of the crystalline interface is necessary.

The structure of a catalytic surfaces can also be affected by processes like sintering. Sintering is the fusion of single particles to form larger ones, as the energetic stage of single small particles (e.g. in powders) is unfavorable due to the high surface area and consequentially the high surface energy. Hence, particles fuse together in order to minimize the free energy. This process is particularly relevant at high temperatures, due to enhanced diffusivity [27]. Due to the anisotropy at the grain boundary, caused by a mismatch of the crystal lattices at the interface between the grains, the orientation of single grains during this process will determine the temporal evolution and final

morphology of the fused particles.

This thesis attempts to model microstructural evolution using phase field methods, a thermodynamic based model to solve interfacial problems. Particular relevance is given to the aspect of anisotropy and its consequence on the crystal shape evolution and on the sintering processes. Simulations will be carried out using MOOSE Framework (Multiphysics Object-Oriented Simulation Environment), an open-source, parallel finite element framework. This framework includes a *phase field module* that offers a base for phase field calculations.

2 Background

2.1 Microstructure simulation with phase field methods

Phase field methods have emerged as a powerful tool to simulate the microstructure evolution on the mesoscale [11]. One of the most important features of this model is the introduction of a diffuse interface which, in contrast to the classical models, transitions smoothly. In classical models that strictly divide structural or compositional domains using sharp interfaces, explicit tracking of the interface is required to apply physics and boundary conditions. Additionally, numerical issues may occur when interfaces merge or pinch off occurs [11].

On the contrary, diffuse interfaces assume constant values in the bulk while values along the thin interface are continuously interpolated, to describe the transition between phases [23]. The concept of diffuse interface was first introduced by Van der Waals in the end of the 19th century, analyzing the density variation between a liquid and vapor [35]. Decades after which Cahn & Hilliard postulated the same concept. The basic idea is that the local free energy density is not only dependent on the field variable but also on its gradients [10].

Phase field problems are described by a set of conserved and non-conserved variables. Conserved variables have to satisfy the continuity equation and might represent e.g., a concentration. Non-conserved variables can be used to differentiate structures in the domain e.g., representing the orientation of different grains.

Considering a simple system with a single field variable ϕ the total free energy can be described as:

$$F = F_{bulk} + F_{int} = \int_V f(\phi) + \frac{1}{2}k_\phi \nabla \phi^2 dV \quad (2.1)$$

where $f(\phi)$ is the local free energy and k_ϕ the gradient energy coefficient.

The temporal evolution of phase field variables is caused by the variation of the free energy towards a state of equilibrium.

In case of a conserved variable ϕ_i the continuity equation has to be fulfilled, so:

$$\frac{d\phi_i}{dt} = -\nabla\phi_i v \quad (2.2)$$

with v being the local velocity. If only diffusive transport j_{diff} is considered:

$$\phi_i v = j_{diff} = -M_i \nabla\mu \quad (2.3)$$

where $\nabla\mu$ is the chemical potential, being the driving force for the morphological change, and M_i is related to the mobility. If eq. 2.3 is inserted in eq. 2.2 we obtain the evolution equation of the conserved variable (eq. 2.4), the Cahn-Hilliard-equation [9]:

$$\frac{d\phi_i}{dt} = \nabla M_i \nabla\mu \quad (2.4)$$

The expression for the chemical potential is obtained from a functional derivative of the free energy $\mu = \frac{\delta F}{\delta \phi_i}$ (for example from eq. 2.1).

For a non-conserved η_p variable the continuity equation does not have to be fulfilled. In this case the evolution equation is described by the Allen-Cahn-equation [8] (eq. 2.5).

$$\frac{d\eta_p}{dt} = -L_p \nabla\mu \quad (2.5)$$

with L_p being related to the mobility and μ derived from the free energy $\mu = \frac{\partial F}{\partial \eta_p}$.

2.2 Crystal anisotropy

Anisotropy of surface energy plays a fundamental role in the formation and evolution of crystals. A simple approximation of the surface energy in a solid given by $\gamma \approx E_{coh} \frac{Z_s}{Z} N_s$ where Z_s is the number of broken bonds, Z the number of nearest neighbors, E_{coh} the bulk cohesive energy and N_s the areal density of surface atoms [18]. In an fcc atom arrangement the number of nearest neighbors is 12. But, for a $[111]$ -face the number of broken bonds is three ($Z_s = 3$) while for a $[100]$ -face it is four ($Z_s = 4$). So the surface energy differs depending on the orientation of the surface.

In an equilibrium stage, a crystal will orient its faces in a way that the total free energy is minimized. The Wulff-construction is an analytical method to determine the equilibrium shape of a crystal. According to this methodology, starting from a point, vectors in the direction of a face with a length proportional to the face surface energy are constructed.

After this, lines (or areas in 3D) perpendicular to the vectors are drawn. The equilibrium shape can be identified as the smallest area within the intersection of the lines.

Let's assume that the $[10]$ -direction has a surface energy of $0.22 \frac{J}{cm^2}$ and the $[11]$ -direction $0.20 \frac{J}{cm^2}$. We follow the Wulff-construction with h_1 and h_2 being lengths proportional to the surface energies. In this case, it results in two intersecting squares as shown in fig. 2.1. In the equilibrium stage, the crystal will assume the shape represented by this intersection.

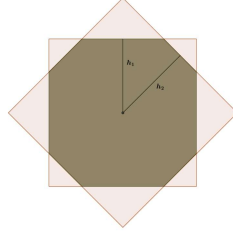


Figure 2.1: Wulff - construction method. The equilibrium shape is represented by the intersection.

Now, let's assume a 2-dimensional crystal with a surface of $1 cm^2$ and we want to calculate the total surface energy as $E = U * \gamma$, with U being the perimeter of the crystal shape. As demonstrated in Fig. 2.2, if we calculate the total energy for a crystal with only $[10]$ -faces ($\gamma_{10} = 0.22 \frac{J}{cm^2}$) this will be $E = 4 * 1 cm * 0.22 \frac{J}{cm^2} = 0.88 \frac{J}{cm}$ while, for a crystal with only $[11]$ -faces ($\gamma_{11} = 0.20 \frac{J}{cm^2}$) $E = 4 * 1 cm * 0.20 \frac{J}{cm^2} = 0.80 \frac{J}{cm}$. But, if we use the crystal described above, which applies the Wulff-method, the total free energy will be $E = 4 * 0.333 cm * 0.20 \frac{J}{cm^2} + 4 * 0.595 cm * 0.22 \frac{J}{cm^2} = 0.78 \frac{J}{cm}$ with the surface area still being $1 cm^2$. The resultant crystal has the form with the least surface energy.

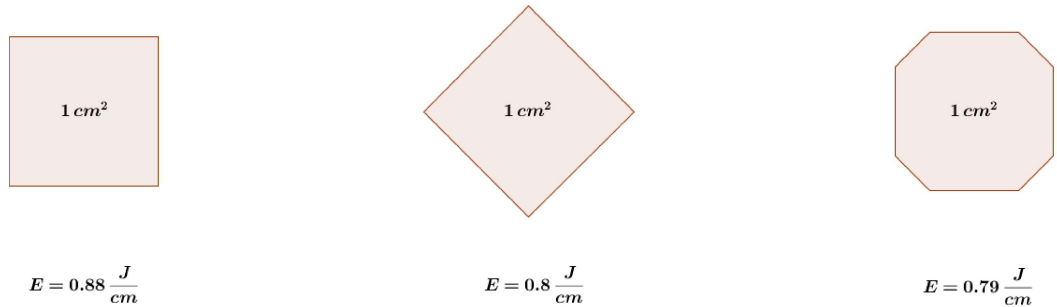


Figure 2.2: Surface energy for different shapes with same cross sectional area. The Shape according to Wulff-construction has the lowest surface energy.

Many reactions are classified as *structure sensitive reactions* as the reaction rates of such reactions are dependent on the orientation and positioning of the atoms on the catalytic surface. Somorjal et al. [30] intensively studied the structure sensitiveness of many reactions using single crystals. For example, they demonstrated that the reaction rate in the synthesis of ammonia (from nitrogen and hydrogen) differs in several orders of magnitude depending on the crystal orientation, while other reactions do not depend on the structure, or the sensitiveness depends on the reaction conditions. Understanding the crystals structure can help in optimizing reaction rates and sensitivities.

Depending on the fluid environment the catalyst microstructure undergoes morphological changes as well. Grunwaldt et al. [17] have observed that steep changes occurs in the structure of Rh/Al_2O_3 catalyst during partial methane oxidation within 100 micrometers due to oxidation of metallic rhodium. Cheula et al. [13] simulated the morphological changes on Rh/Al_2O_3 catalyst during the partial oxidation of CH_4 using a structure-less micro-kinetic to calculate the species molar fractions along the reactor. They used DFT and *ab initio thermodynamics* to determine the most stable bulk and surface structure. The shapes of the crystals were then calculated using Wulff–Kaisheew construction. The results demonstrate strong catalyst microstructure changes along the reactor coordinate and consequentially, in the amount of active sites.

As this thesis aims to track the crystal evolution time dependently using phase field methods, surface energy anisotropy should be incorporated in the phase field equations. Modeling dendritic growth Kobayashi [20] showed that this can be achieved. He formulated the gradient energy coefficient k_ϕ as $k_\phi(\theta)$ where θ is the angle between the order parameter normal vector and the x axis (in 2D simulation). He showed a simple way to define anisotropy as $k_\phi \sim \gamma(\theta)$ with $\gamma(\theta)$ being the anisotropic surface energy. A commonly used expression for anisotropy in 2D is $\gamma(\theta) = (1 + \delta \cos(j\theta))$, with δ being the anisotropic strength and j the number of minima of the sinusoidal function. A value of 3 for j would lead to a 3-folded crystal, a value of 4 to a 4-folded and so on. In the case of $\delta = 0$ the system is isotropic.

In order to model complex crystal morphologies a complex description of $\gamma(\theta)$ is required. Extensive research data on surface energy for different materials and orientations are available. Nevertheless, in order incorporate it in the model, a continuous description of the discrete data is necessary. A generic expression is proposed by [28]

$$\gamma(\bar{n}) = \gamma_0 \left(1 - \sum_1^N \alpha_i (\bar{n} \bar{m}_i)^{w_i} \Theta(\bar{n} \bar{m}_i) \right) \quad (2.6)$$

where \bar{n} is the phase normal vector, \bar{m}_i are the vectors that give the minima of the surface energy, N is the total number of minima with depth α_i , w_i controls the width of

each minimum and Θ is the Heaviside step function.

Other approaches have been developed, for example, for fcc and bcc metals [24] and hcp metals [25], in which the continuous formulation of the anisotropic energy is dependent on four parameters that can be computationally or experimentally determined. In [22] the anisotropic solid/liquid interface energy of bcc crystals for different reduced temperatures has been described using a Kubic harmonic fit.

Salvalaglio et al. [28] simulated the evolution of spherical particles towards their equilibrium shape using phase field methods with a surface energy description according to equation 2.6. For the simulation the FEM toolbox AMDiS [36] was used. They employed a Cahn-Hilliard equation for strong anisotropy as proposed by Torabi et al. [34], according to which the free energy function assumes the form:

$$F(\phi) = \int_V \gamma(\mathbf{n}) \left(\frac{1}{\epsilon} f(\phi) + \frac{\epsilon}{2} |\nabla \phi|^2 \right) dV \quad (2.7)$$

with f being the double-well potential and ϵ the interface width and ϕ being the conserved variable.

The evolution equation of the conserved variable ϕ has the form:

$$\frac{d\phi}{dt} = \nabla \cdot (M \nabla \mu) \quad (2.8)$$

with μ being the chemical potential and M the mobility.

The chemical potential can be obtained as:

$$\mu = \frac{\delta F}{\delta \phi} \approx -\epsilon \nabla \cdot [\gamma(n) \nabla \phi] + \frac{1}{\epsilon} \gamma(n) f'(\phi) - \epsilon \nabla \cdot [|\nabla \phi|^2 \nabla \gamma(n)] \quad (2.9)$$

The anisotropic Cahn-Hilliard equation is then a 4th order PDE.

If anisotropy is strong, sharp corners are formed and the anisotropic Cahn-Hilliard equation is ill-posed [34]. In this case a regularization is needed. By considering, for example, a Willmore regularisation, higher order terms are added to the free energy description to remove ill-posedness [33]. The regularized anisotropic Cahn-Hilliard equation would then be a 6th order PDE.

2.3 Sintering

Thermal degradation due to high temperatures also plays a fundamental role in catalytic decay [2]. One of the most important phenomena in this context is sintering, the fusion

of particles across boundaries resulting in a single particle, leading to a reduction of active surface.

A first study of phase field simulation of sintering was conducted by Wang et al. [37] where sintering of particles was simulated using a conserved variable to describe the concentration field and non-conserved variables to distinguish single particles, simultaneously solving Cahn-Hilliard and Allen-Cahn equation coupled by a Landau type energy function (depending on conserved and non conserved variables). A scalar mobility function was used, depending on the phase field variables, to activate different types of diffusion at different locations in the grain (surface, vapour, volume, grain boundary diffusion). In addition, Yang modified the evolution equations by adding an advection term, considering convective material transport caused by rigid body motion, due to particle interaction forces. Chockalingam et al. [14] applied phase field methods to simulate silver particles sintering using finite element methods in MOOSE Framework. To obtain quantitative results, parameters of the free energy functional were derived from material property parameters according to [1] (grain boundary energy, surface energy and grain boundary width). To consider the anisotropy of diffusion phenomena, a tensorial description of the mobility was adopted, so that diffusive transport depends on the orientation of the phase field variables.

Extensive studies of particle sintering using MOOSE Framework have been conducted by the research group of Biswas et al. [3] [4] [5] at Idaho Laboratories. The publication of Biswas et. [5] studied the role of grain boundary anisotropy in particle sintering. Grain boundaries are the internal interfaces between the grains, with an excess of free energy per unit area. The grain boundary energy is anisotropic, since depending on the misorientation of the lattice and the orientation of the grain boundary plane, boundaries can assume different microscopic structures [26]. Biswas et. al [5] employed the 5 DoF-model proposed by Boutalov et al. [7], which permits to calculate the grain boundary energy based on Euler angles (three DoF for grain boundary misorientation and two for inclination). They also developed an algorithm to update the Euler angle, which changes due to rigid body motion, to update the grain boundary energy. The role of grain boundary anisotropy has previously been implemented using more simple models in case of simulation of grain growth [19]. In this work the grain boundary energy depending on grain boundary inclination angle ϕ and misorientation angle θ proposed by Read and Schockly [32] has been used. For small tilt angles ($\theta < 20^\circ$) grain boundary energy can be described as: $\gamma_{gb} = \gamma_{gb0}(\sin(\phi) + \cos(\phi))\theta(1 - \ln(\theta))$ with γ_{gb0} being constant.

Even though sintering has already been vastly analyzed, particularly using MOOSE Framework, the cited publications did only simulate using spherical particles and with-

out taking into account the anisotropy of the surface energy.

Salvalaglio et al. [29] used phase field theory to simulate the coalescence of Ge microcrystals on Si substrate at high temperatures taking surface energy anisotropy into account. In this work first the evolution of the crystal to their equilibrium state was simulated, further on coalescence of multiples crystals was archived by enhancing diffusivity.

2.4 MOOSE Framework

Simulations will be carried out using the finite element framework called MOOSE-Framework (Multiphysics Object - Oriented Simulation Environment) developed at Idaho National Laboratory. MOOSE allows a massive parallel performance solving strong nonlinear system in a full coupled manner [16]. One of the main features of MOOSE is the modularised structure using *kernels*. *Kernels* represent a piece of "physics", a mathematical operator that represents a term in a PDE. This structure allows to easily swap or couple different *kernels* to solve new problems. Additionally MOOSE offers adaptive methods like mesh adaptivity. This is particularly convenient in interfacial problems, where steep changes at the interface might have better resolution with a mesh refinement. MOOSE Framework has an already implemented phase field module, with numerous *kernels* and material properties that are relevant to solve problems with phase field methods.

3 Scope of this research

Scope of this thesis is to gain deeper insight in relevant microstructural processes using phase field model, focusing on the surface energy anisotropy. This study will first concentrate on the temporal evolution of crystals towards an equilibrium shape, following which the sintering of grains from the equilibrium stage will be simulated (fig. 3.1). All simulations will be carried out using MOOSE Framework. In order to be able to describe anisotropy new *kernels* may have to be implemented, which requires C++ object oriented coding. The models used will be based on previous researches. Main priority is given the simulation of crystal evolution towards an equilibrium status, analyzing the effect of changes in the energy anisotropy description. After this sintering of multiple grains will be simulated in the easiest manner. If time permits other effects like: anisotropy of the grain boundary energy, tensorial anisotropic diffusion and grain rigid body motion, should be explored.

Given that the thesis focuses on the applicability of MOOSE Framework on the desired models and computational power is limited, simulations will be in 2-dimension.

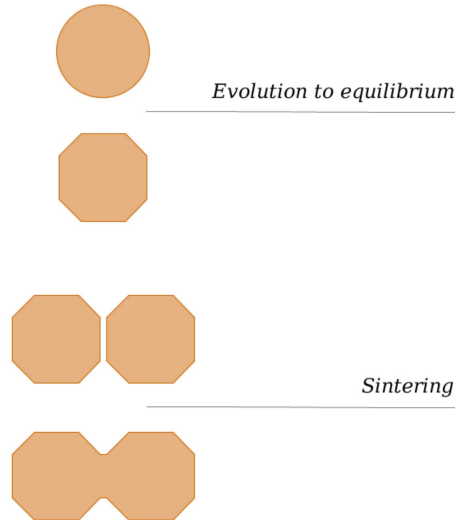


Figure 3.1: Sequence of simulations in this thesis.

4 Timeline

This timeline has been revised: see 5.

- **04.05.20 - 01.08.20**

- Simulation of single crystal evolution towards equilibrium**

- 04.05.20 - 17.05.20

- * Revision of the phase field module in MOOSE Framework with using the already implemented *kernels*
 - * Revision of code and structure of *kernels*
 - * Finalize mathematical model to be applied for implementation of anisotropic surface energy

- 18.05.20 - 31.05.20

- * Implementation of the model for single crystal evolution in MOOSE Framework

- 01.06.20 - 14.06.20

- * Test the model with simple geometry
 - * Test the model on MOOSE Framework and adapt simulation conditions to improve performance
 - time scaling
 - mesh dimensions
 - adaptivity
 - scaling of parameters to improve convergence
 - ...

- 15.06.20 - 04.07.20

- * Improvement of model (for example implementation of a regularization of anisotropic evolution equation)

- 05.07.20 - 18.07.20
 - * Test the model with simple geometry
 - * Test the model on MOOSE Framework and adapt simulation conditions to improve performance
 - time scaling
 - mesh dimensions
 - adaptivity
 - scaling of parameters to improve convergence
 - ...
- 19.07.20 - 01.08.20
 - * Simulation of anisotropic crystal evolution with variation of model parameters:
 - observe effects on equilibrium shape and compare with shape according to Wulff
 - observe effect on temporal evolution (like duration till equilibrium)
- **02.08.20 - 19.09.20**
Simulation of sintering
 - 02.08.20 - 15.08.20
 - * Simulation of sintering of spherical particles under isotropic conditions
 - * Find way to simulate sintering of multiple grain from an equilibrium stage
 - Construction of geometries according to Wulff's -construction or
 - Possibility of using output file from previous simulation (sphere to equilibrium crystal)?
 - * Find appropriate description of mobility in order to enhance sintering
 - 16.08.20 - 29.08.20
 - * Develop an easy model to test possible implementation
 - * Test the model on MOOSE Framework and adapt simulation conditions to improve performance
 - time scaling
 - mesh dimensions
 - adaptivity

- scaling of parameters to improve convergence
 - ...
- 30.08.20 - 05.09.20
 - * Simulation of anisotropic crystal sintering with variation of parameters and crystal geometries
 - observe effects on equilibrium shape
 - observe effects on temporal evolution (like duration till equilibrium)
- 05.09.20 - 19.09.20 Additional Work
 - * Simulation of a more detailed sintering model taking into account:
 - advection force
 - rigid body motion
 - anisotropy of mobility
 - anisotropy of grain boundary energy
- **20.09.20 - 01.11.20**
Thesis
 - 20.09.20 - 01.11.20
 - * write thesis

5 Correction of Timeline

Since a new FEM - Simulation Framework *PRISM-PF* [15] has been chosen to carry out this thesis, the previously proposed timeline changes.

The project is divided in the following topics. The timeline is represented in fig. 5.1.

T1: Modelling of crystal anisotropy.

- find appropriate mathematical model to implement anisotropy in the kinetik equations.
- 2D and 3D simulations of facetting crystals taking the anisotropic behaviour of platinum as example.
- simulation of crystals with surface energy data from DFT-Simulations (Density functional theory) -> Effect of different gas atmospheres on the shape of platinum
- comparison of the equilibrium shape with Wulff-shape
- postprocessing: time evolution of the relative facet orientations

T2: Simulation of sintering of spherical particles

- implementation of common models for isotropic sintering acc. to [37] (Wang et al.)
- short study on the effect role of tensorial mobility.
- implementation of anisotropic grain boundary energy in the easiest manner (effect of the grain misorientation on the grain boundary orientation)
- implementation of grain advection and rigid body motion
- optional: Coupling of rigid body motion with grain boundary energy (Angle update)

T3: Simulation of sintering of crystals

- 3D simulation of sintering of crystals from an equilibrium shape with different orientations in space.
- 3D simulation of sintering of crystals from an equilibrium shape with different orientations in space taking into account grain boundary anisotropy in the easiest

manner (as done for spherical particles)

- optional: implementation of grain advection and rigid body motion as well as coupling with grain boundary energy
- optional: study on the role of anisotropic mobility

T4: Write thesis

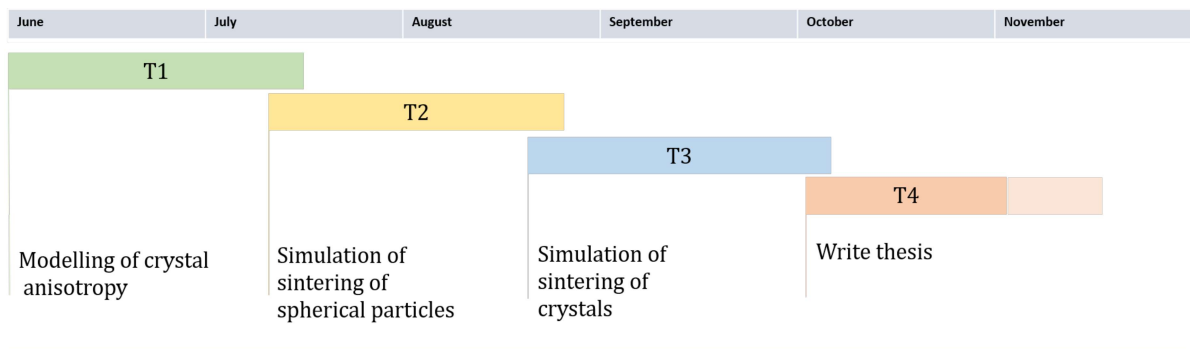


Figure 5.1: Timeline.

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