

# A Novel Physics Node for Nakamura Crystallization Kinetics

Levy, Arthur\*

\*Laboratoire de Thermocinétique de Nantes, Nantes, France

\*Corresponding author: rue Christian Pauc, 44306 Nantes Cedex3, France, Arthur.levy@univ-nantes.fr

**Abstract:** Crystallization phenomena are of first interest in several industrial applications (polymer forming processes, metallurgy, phase change flow, energy storage...). A classical way to model the crystallization evolution is using the Nakamura kinetics law.

In this paper, a novel physics is developed using the COMSOL physics builder and accounts for the resolution of this Nakamura kinetics. The new physics can be used in any COMSOL multiphysical model. An example of composite forming simulation, which includes the coupling with a heat transfer node is presented.

The new physics is efficient at automatically handling couplings (with built-in physical magnitudes) but also calls for physical material properties with consistent units. Thus, using this novel physics will prevent mistakes when developing new models.

**Keywords:** Physics builder, Crystallization kinetics, Heat transfer, coupling, Nakamura, robust time integration.

## 1. Introduction

### 1.1 Thermoplastic polymer forming

Thanks to their good specific properties, advanced polymers and their composite materials tend to replace traditional materials such as metallic materials in the industry. Thermoplastic polymers and their composites offer new possibilities for the industry. Large structures can be processed rapidly and more cost-effectively than when thermoset are used, since the latter need to undergo lengthy curing reactions. Advanced thermoplastic composites very often have a semi-crystalline matrix. This is the case for PET, or polyamide but also, for advanced polymers such as PAEK. In that case the cooling, solidification and final properties are ruled by the crystallization phenomenon, which is usually thermally induced [1].

### 1.2 Predicting crystallization

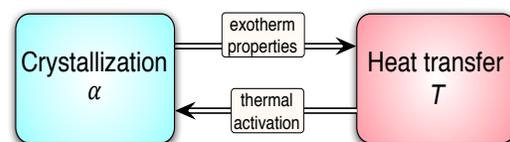
For these materials, crystallization, that occurs during the forming process, and especially during the solidification phase, plays a critical role in the final part quality. For instance, in the case of injection moulding, crystallization determines the liquid / solid transition and thus rules the ejection criteria. In addition, crystallization induces shrinkage and residual stresses.

Therefore, polymer forming simulation software have to accurately predict crystallization effects. Especially during the cooling phase. An accurate quantitative prediction is a prerequisite for predicting solidification (or gel) time.

Crystallization depends on both temperature and flow histories. Classically at the macroscopic scale, one defines a scalar variable, the degree of crystallization, which quantifies the advancement of the crystallization transformation and varies between 0 and 1.

### 1.3 Paper outlines

In this paper, a novel physics is developed in COMSOL using the **physics builder**. It contains the crystallization rules presented in section 2. We focus on the thermal quiescent crystallization. Indeed, temperature history appears to play the dominant role in crystallization effects, in forming processes. By essence this problem is thus **multiphysical** since heat transfer and crystallization effects both have to be predicted simultaneously (see Figure 1). A typical model, including a heat transfer node and the newly developed crystallization node, is then developed in COMSOL (section 4).



**Figure 1.** Heat transfer and crystallization coupling is a classical multiphysical problem when dealing with solidification of semi-crystalline polymer.

## 2. Robust modeling of polymer crystallization

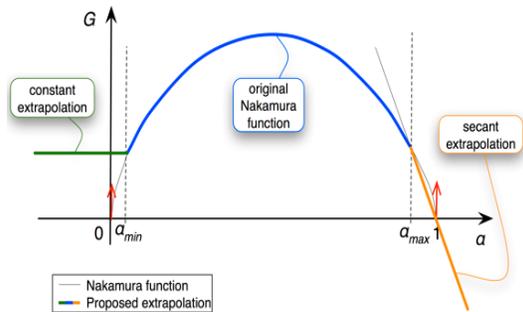
### 2.1 Crystallization kinetics

Evolution of the degree of crystallization  $\alpha$  is ruled by the crystallization kinetics. First kinetics models were based on geometrical, nucleation and growth rate assumptions [2]. Nakamura [3] extended these models to account for non-isothermal conditions. The Nakamura law is written:

$$\frac{d\alpha}{dt} = K(T) \times \underbrace{n(1-\alpha)[- \ln(1-\alpha)]^{1-\frac{1}{n}}}_{G(\alpha)} \quad (1)$$

where  $t$  is the time,  $n$  is the Avrami index and  $K(T)$  is the Nakamura kinetics crystallization function which is related to the Avrami isothermal kinetics function  $K_{Avrami}(T)$  by  $K(T) = K_{Avrami}(T)^{1/n}$ . In the following, the function  $G(\alpha)$  is called *Nakamura function*. It is represented in Figure 2.

The Nakamura crystallization kinetics is very widely used to predict advancement of the crystallization transformation in polymer forming processes [1, 4, 5, 6, 7].



**Figure 2.** The original Nakamura function  $G$  (eq.1) is singular when  $\alpha=0$  and when  $\alpha=1$  (vertical tangent, represented by the red arrows). In the proposed modified extrapolation, a thresholding is performed below  $\alpha_{min}$ , and a linear extrapolation above  $\alpha_{max}$ .

### 2.2 Modified Nakamura kinetics

Nakamura function  $G$  presents singular derivative at the vicinity of  $\alpha=0$  and  $\alpha=1$ . Therefore, a modification of the Nakamura function is proposed by extrapolating it below

$\alpha_{min}=10^{-6}$  and above  $\alpha_{max} =1-10^{-6}$ . These modifications, discussed in a recent work [8], are illustrated in Figure 2. They ensure:

- (i) a robust numerical integration by forcing real values of  $G$  when  $\alpha$  is not in the interval  $[0,1]$ , and
- (ii) forces an artificial germination when  $\alpha=0$ .

### 2.3 Heat transfer coupling

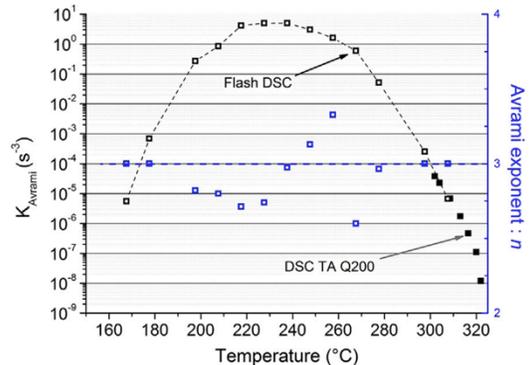
In real industrial process, as illustrated in Figure 1, the coupling of crystallization kinetics and heat transfer is of first interest. Crystallization kinetics and its domain dependent variable  $\alpha$  is strongly coupled to heat transfer and its domain dependant variable : the temperature  $T$ .

On the one hand, crystallization is an exothermic reaction such that a source term

$$Q = \rho_m \phi_m H \frac{d\alpha}{dt} \quad (2)$$

appears in the heat transfer equilibrium equation,  $\rho_m$  being the material density (matrix density in case of a composite)  $\phi_m$  the volume content of matrix and  $H$  the enthalpy of crystallization. Moreover, thermal properties (conductivity, density and specific heat) depend on the degree of crystallization. These dependencies are imposed by the material behaviour.

On the other hand, temperature appears as a driver to the crystallization kinetics. It appears explicitly with the Nakamura kinetics crystallization function  $K(T)$  in equation 1. This function is also temperature dependent. A typical example for PEEK is given in Figure 3.



**Figure 3.** Avrami kinetics crystallization function  $K_{Avrami}$  and Avrami index  $n$  versus temperature for PEEK polymer, as characterized by Tardiff et al [9].

### 3. Implementation of a dedicated physics in COMSOL

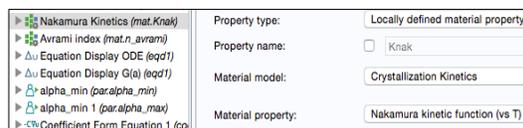
In a physical domain, the degree of crystallization  $\alpha$  has to be solved for at each location in space. The ruling ODE (eq. 1) could be implemented in any COMSOL model using the domain ODE node. After having done so for several years, with multitude of models, we decided to implement this Nakamura kinetics in a novel physics node, using the physics builder in COMSOL. First, this enables to implement once and for all the Nakamura function modification (see Fig. 2). Then, it simplifies eventual coupling with heat transfer (exotherm computation, for instance). And finally, it eases the creation of new models by providing readily available physical material properties (see Fig. 3). In addition, all the variables now have physical names and consistent units. This prevent mistakes while developing new models.

#### 3.1 Domain and dependent variable

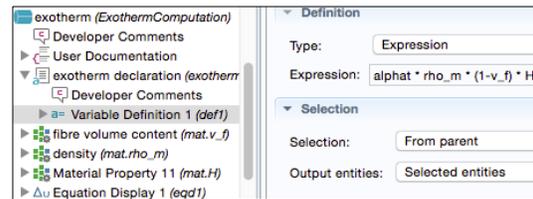
The Nakamura kinetics equation (1) has to be solved at each material location to obtain the field of degree of crystallization  $\alpha$ . Thus,  $\alpha$  is defined as the **dependent scalar variable** over a domain which **dimension** can be either 0, 1, 2 or 3D. A *Crystallisation* domain feature node is added in the physics builder as the default node.

#### 3.2 Material properties and user input

Equation (1) calls for two material properties, the Avrami index  $n$  and the Nakamura kinetics function  $K$ . These two new material properties are added in the physics builder (see figure 4). Note that the user will eventually have to input the thermal dependency of  $K$  in the model (for an example see section 4). In terms of parameter input for the Nakamura model, only two scalars,  $\alpha_{\min}$  and  $\alpha_{\max}$ , are required.



**Figure 4.** Specific material properties appearing in the Nakamura law (1) are implemented in the physics builder.



**Figure 5.** Exotherm computation is automated by adding a domain feature node. This node only performs exotherm computation and does not require any input.

The exotherm  $Q$  (eq.2) can be computed automatically. This is performed in the physics builder by adding a domain feature node that includes the domain variable *exotherm*. In addition to this node, two new material properties ( $\rho_m$  and  $\phi_m$ ) are needed (see figure 5).

#### 3.4 Coefficient form PDE

The right hand side of equation (1) is implemented by adding a new domain variable RHS. Then, the ordinary differential equation (1) is solved for, by adding a coefficient form equation in the physics builder.

The newly developed physics is then added in the local physics library using the physics manager. It is now readily available to the COMSOL user to be added in multiphysical model.

### 4. Application: simulating the cooling of a thermoplastic composite plate

In this section, the quiescent cooling of a thermoplastic composite square is modeled in COMSOL. Heat transfer is handled using a heat transfer node whereas crystallization physics is added using the newly developed node. Full coupling shown in Figure 1 is taken into account.

#### 4.1 Modelling

A square of dimension 2x2cm is sketched in a 2D model in COMSOL.

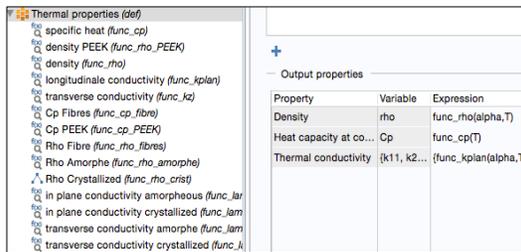
**Heat transfer.** Standard heat transfer in solid node is added. Thermal material properties are adapted from the literature and model an orthotropic Carbon/PEEK composite [4,9,10]. Thermal material properties depend on

temperature and degree of crystallization (see fig.6). Classically, the properties are characterized versus temperature for amorphous ( $\alpha=0$ ) and fully crystalline ( $\alpha=1$ ) states. A mixture law is then used to get thermo- and crystallo- dependent properties.

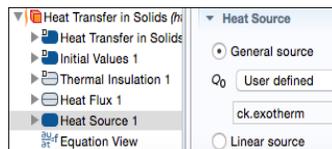
An initial temperature of 300°C is imposed in the whole domain. Symmetry is imposed on the left and lower boundaries. A convective heat flux to an external temperature of 230°C with an exchange coefficient  $h=20\text{Wm}^{-2}\text{K}^{-1}$  is considered on the upper and right boundaries. The heat source arising from the crystallization exotherm is also added automatically by calling the *exotherm* variable (see Figure 7).

**Crystallization.** The crystallization node is added in the model and enables for the resolution of the Nakamura crystallization kinetics at each point.

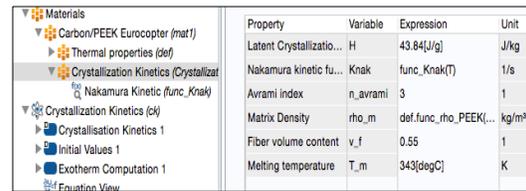
The missing material properties automatically appears in the material node (see Figure 8). Values from the literature [9] were implemented. Note that the temperature dependency is accounted for here.



**Figure 6.** Thermal material properties depend on temperature and degree of crystallization. For an ease of implementation, material « functions » are extensively used.



**Figure 7.** Exotherm variable is directly called in a heat source node and prevents mistakes while developing new models.



**Figure 8.** Material properties related to the crystallization kinetics automatically appear with the right units in the material node. Temperature dependency is to be implement here by the model user.

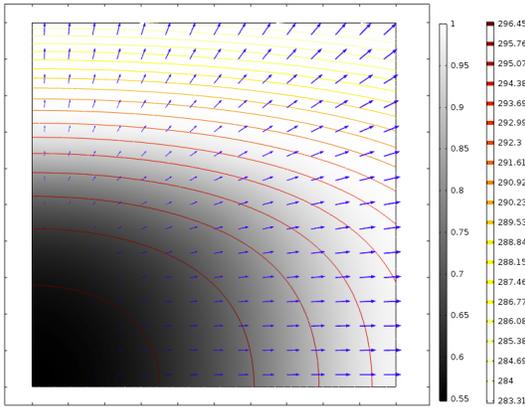
An initial value of the degree of crystallization is set to 0 in the whole domain and models an initially fully molten material. Note that even if imposing  $\alpha=0$ , crystallization will be initiated artificially thanks to the non-zero value of  $\alpha_{min}$ . Exotherm computation domain feature is also added for a fully coupled resolution as depicted in Figure 1.

**Mesh and resolution.** A default triangular mesh using “fine” size is used. The time dependant study is performed between 0 and 150 s. Solutions are stored every 10 seconds.

The solving methods are the default ones proposed by COMSOL except that a maximum time stepping of 1 s is imposed in the time dependant solver. Indeed, crystallization is an event that will occur while cooling the material down. Large time stepping may result in missing this event. A correct time stepping, featuring automatic time stepping with a maximum time step size, is thus required [4].

## 4.2 Results

Temperature and degree of crystallization fields are obtained versus time. This information are shown in figure 9 at time  $t = 90$  s. They prove very useful to better understand a forming process (such as injection or compression moulding for instance). In particular, of interest is the time at which the material is crystallized to the core. This corresponds to the time when the material is fully solid. This is the end of the forming phase and the part can eventually be ejected [11].



**Figure 9.** Prediction of the cooling and solidification of a composite plate. The surface plot represents degree of crystallization, the lines are isothermals and the arrows heat flux. Plot is at time  $t=90s$ .

### 4.3 Discussion

The novel *crystallization* physics node proves useful at efficiently implementing a coupled heat transfer and crystallization problem. Nonetheless, some numerical considerations should be discussed.

First the above resolution is efficient and accurate because the crystallization transition zone is wide compared to the mesh and part size. In the case of thick or large geometries and/or faster cooling cycles, crystallization fronts may appear. An accurate modelling of such a sharp transition zone would require **automatic remeshing method**, as described in [4]. This is possible to implement in COMSOL but we are waiting for future versions to provide a better remeshing algorithm.

Then, the present test case considers a quiescent material. In the case of flowing material, a **convection** term should be added to eq. 1 and the coefficient form PDE (section 3.4) and may require special care to ensure stability.

### 5. Conclusions

Thermal crystallization is a phenomenon that appear in several multi-physical applications (forming processes, phase change flow, energy storage...). An accurate modelling of the crystallization (solidification) phenomenon is thus required. The **Nakamura law** is a standard **crystallization kinetics**.

In the presented work, a novel physics was implemented using the **physics builder** in

COMSOL and solves for the Nakamura crystallization (a local ordinary differential equation). The new physics node can be used in any time dependent 0,1,2 or 3D multiphysical COMSOL model. It enables to compute the field of degree of crystallization versus time.

The use of this new physics was illustrated in a model example of the **cooling and solidification** of a thermoplastic composite part.

### 6. References

1. N. Boyard, *Heat Transfer in Polymer Composite Materials: Forming Processes*, John Wiley & Sons (2016)
2. M. Avrami, Kinetics of Phase Change. I General Theory, *The Journal of Chemical Physics*, Vol. 7, p. 1103 (1939)
3. K. Nakamura et al., Some Aspects of Nonisothermal Crystallization of Polymers. I. Relationship between Crystallization Temperature, Crystallinity, and Cooling Conditions, *Journal of Applied Polymer Science*, Vol. 16(5), p. 1077 (1972)
4. A. Levy et al., Heat Transfer and Crystallization Kinetics in Thermoplastic Composite Processing . A Coupled Modelling Framework, In ESAFORM 19, Nantes, France (2016)
5. B. Pignon et al., A New PvT Device for High Performance Thermoplastics: Heat Transfer Analysis and Crystallization Kinetics Identification, *Polymer Testing*, Vol. 45, p. 152 (2015)
6. A. Amado et al, Characterization and Modeling of Non-Isothermal Crystallization of Polyamide 12 and Co-Polypropylene during the SLS Process, In 5th International Polymers & Moulds Innovations Conference. pp. 207, Ghent, Belgium (2012)
7. R. Le Goff et al., Study and Modeling of Heat Transfer during the Solidification of Semi-Crystalline Polymers, *International Journal of Heat and Mass Transfer*, Vol. 48(25-26), p. 5417 (2005)
8. A. Levy, Robust numerical resolution of Nakamura crystallization kinetics, *International Journal for Numerical Methods in Engineering*. **Under review**
9. X. Tardif, et al. Experimental study of crystallization of PolyEtherEtherKetone (PEEK)

over a large temperature range using a nano-calorimeter. *Polymer Testing*, Vol. 36 pp.10–19.

10. M. Thomas, et al. An experimental device for the simultaneous estimation of the thermal conductivity 3-D tensor and the specific heat of orthotropic composite materials, *International Journal of Heat and Mass Transfer*, Vol. 53(23-24), pp. 5487-5498. (2010).

11. B. Landry & P. Hubert. Experimental study of defect formation during processing of randomly-oriented strand carbon/PEEK composites. *Composites Part A: Applied Science and Manufacturing*. Vol. 77, pp 301-309. (2015).

## **7. Acknowledgements**

The author would like to thank all of his colleagues at LTN for the fruitful discussions concerning thermo-kinetics coupling. Special thanks goes to Steven le Corre, Vincent Sobotka, and Didier Delaunay.