

## **Modelling the interactions between heat conduction, mass diffusion and plasticity**

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### **Résumé**

Un modèle macroscopique est proposé dans le but d'appréhender le comportement de polymères sous hautes températures et pression fluctuante de gaz. De type standard généralisé, il est construit dans le cadre de la thermodynamique des processus irréversibles sous l'hypothèse de petites perturbations. Le volume élémentaire est considéré comme un mélange classique, chimiquement inerte de polymère et de gaz. Les équations constitutives sont détaillées dans le cas d'un comportement mécanique élasto-plastique avec écrouissage isotrope et cinématique linéaire. Notre but est de rendre compte, par un modèle simple et prospectif, des interactions entre phénomènes thermiques, diffusifs et mécaniques associés à une décompression explosive.

### **Abstract**

A macroscopic continuum formulation is proposed in order to describe the behaviour of a class of structural polymers under high temperatures and fluctuating pressure of gas. It is developed in the framework of thermodynamics of irreversible processes with generalized normality rule and small perturbations assumption. The elementary volume is treated as a classical non-reacting mixture of polymer and gas. The constitutive equations are detailed for a mechanical behaviour restricted to plasticity with kinematic and isotropic hardening. Our purpose is to introduce a simple way of accounting for the interrelations between thermal, diffusion and mechanical phenomena acting during an explosive decompression.

## **1. INTRODUCTION**

In some engineering applications, polymer materials are faced with a harsh chemical environment. It is the case when they are used as piece of equipment, such as gaskets or sheaths, for oil/gas transport. They are then exposed to gas pressure so high that some molecules of gas penetrate and diffuse into them. Moreover, the thermal conditions in which these structures are employed generate strong gradients of temperature. Due to the combined effects of mass diffusion, heat transfer and mechanical stresses, the behaviour of such structures is strongly affected, so that irreversible damage generally appears, particularly during the so-called explosive decompression stages associated with oil extraction (this last one is not made at a steady rate but in starts and stops, which induces repetitive drops in pressure, around several mega-Pascal range). With the aim of controlling the in-service behaviour of such structures, it is essential to consider all the interactions existing between thermal,

diffusion and mechanical phenomena. Numerous experimental works have been made on this explosive decompression process, dealing principally with elastomers [1, 2] and more recently with semi-crystalline polymers [3]. However, the models proposed until now are often semi-empirical and involved with limited domain of validity [4]. Moreover, they do not take account of all the possibilities of coupling. The main difficulty of such modelling lies in the fact that coupling operates at two levels. The behaviour of polymers is first sensitive to the thermal and diffusion history. This effect referred as indirect takes place through the expression of each material parameter as a function of both temperature and gas concentration. The response of the structure can also be influenced by another coupling, which is commonly termed direct coupling and can be associated with dissipative phenomena during transient stages (like explosive decompression) for instance. Constitutive equations have then to be written so that such effects could be reported.

In this paper, a simple and prospective model is proposed with the aim of describing the thermo-diffuso-mechanical behaviour of polymers, i.e. with the aim of predicting the thermal state, gas intake and stresses of such materials. The Elementary Volume (EV) is considered as a homogenous non-reacting mixture of polymer and gas. Moreover, it is defined as an open domain exchanging heat, work and material with its surroundings. We opt for the formal framework of internal variables formalism with the generalized normality rule [5]. The choice of the internal variables is governed not only by the intrinsic properties of the system but also by the nature of the studied process [6]. Being interested principally by the instantaneous response of such structures to explosive decompression, the viscous component generally associated with such class of materials is not taken into account in this modelling. So, the mechanical behaviour is considered in the case of small perturbations as elastic-plastic with linear kinematic and isotropic hardening and without damage. The general thrust of this work is to give a formulation as simple as possible of the direct, as well as indirect couplings. It will lead us to discuss the possibility of linking thermal, diffusion and mechanical phenomena together and to evaluate rapidly the effect of such couplings. The set of local balance equations and resulting constitutive laws is detailed hereafter.

## 2. LOCAL BALANCE EQUATIONS

According to the *classical theory of mixtures* [7], the local forms of balance equations are proposed in regular points of the non-polar body. Note that except for the mass balance, the mixture is considered as a whole.

### 2.1. Mass balance

The mass of each constituent of the mixture is conserved at any time, which produces two balance equations linked together. Only the one concerning the gas, i.e. the local equation of diffusion, is detailed below:

$$\rho \dot{Y}_g = - \operatorname{div} J_g \quad (1)$$

where  $\rho$  is the average mass density of mixing,  $Y_g$  the mass fraction of gas present in the mixture and  $J_g$  is the relative mass flux of gas. Note that  $\dot{\phantom{x}}$  represents the time derivative and  $\operatorname{div}$  the divergence operator.  $Y_p$  being the mass fraction of polymer, the following relation is verified at any time:

$$Y_g + Y_p = 1 \quad (2)$$

### 2.2. Momentum balance

The decompression is ‘explosive’ with regard to the diffusion (not mechanical) process. Inertia effects being neglected, the balance of linear momentum pertaining to the mixture collapses to the equilibrium equation:

$$\operatorname{div} \sigma + \rho f = 0 \quad (3)$$

in which  $f$  is the specific external body force for the mixture and  $\sigma$  denotes the Cauchy stress tensor acting on it. Note that the same force  $f$  is applied on both gas and polymer.

### 2.3. Energy balance - First principle

The first principle of thermodynamics accounts for the conservation of the energy, which implies:

$$\rho \dot{u} = \dot{\varepsilon} : \sigma - \operatorname{div} J_T + r \quad (4)$$

where  $u$  is the specific internal energy of the gas-polymer system,  $\varepsilon$  the infinitesimal strain tensor associated with the mixture,  $J_T$  the heat flux and  $r$  the external heat supply per unit volume.

### 2.4. Entropy balance - Second principle

#### 2.4.1. Accompanying local state - Gibbs relation

The assumption of a local accompanying state allows us to describe at any time the state of a given material EV by a set of state variables. We admit first the existence of one homogeneous absolute temperature  $T$  valid for the mixture and for all its constituents. Moreover, in small deformation, total strain is classically separated into elastic and inelastic components, denoted  $\varepsilon^e$  and  $\varepsilon^p$  respectively. Finally, the classical theory of plasticity assumes the existence of a yield surface in the stress space. The aging effects being neglected, two internal variables are introduced to describe the kinematic and isotropic hardening, namely a rank-two tensor  $\alpha$  and a scalar  $p$ . Their dual variables are represented by  $X$  and  $A$  respectively. The state variables chosen for characterizing the EV are thus the temperature, the elastic strain, the mass fractions of gas and polymer and the two above internal variables.

The specific entropy  $s$ , linked to such an element, is then expressed as a homogenous function of the following extensive parameters:  $u$ ,  $\varepsilon^e$ ,  $Y_g$ ,  $Y_p$ ,  $\alpha$  and  $p$ . In the framework of open systems, the fundamental Gibbs equation is assumed valid [5], which yields the form:

$$T \dot{s} = \dot{u} - \frac{1}{\rho} \sigma : \dot{\varepsilon}^e - \Delta\mu \dot{Y}_g + A \dot{p} + X : \dot{\alpha} \quad (5)$$

in which according to the relation (2), only the mass fraction of gas appears, more exactly its rate of change. The term in product is the difference between the chemical potential of gas and the one of polymer [ $\Delta\mu = \mu_g - \mu_p$ ]. It becomes thus a driving force for the evolution of gas concentration of the system.

#### 2.4.2. Volume dissipation – Fundamental inequality

Using the two foregoing equations (4, 5) combined with the partition of the total strain, one defines locally the usual rates of change of entropy due to external exchanges (6-a) and internal evolutions (6-b). Note that  $J_s$  designates the entropy flux (6-c) and  $\nabla$  the gradient operator.

$$\rho \dot{s}_e = -\text{div} J_s + \frac{r}{T} \quad \rho \dot{s}_i = \frac{1}{T} \sigma : \dot{\varepsilon}^p + \frac{\rho}{T} [A \dot{p} + X : \dot{\alpha}] \quad J_s = \frac{1}{T} J_T - \frac{\Delta\mu}{T} J_g \quad (6)$$

$$+ J_T \cdot \nabla \left[ \frac{1}{T} \right] - \nabla \left[ \frac{\Delta\mu}{T} \right] \cdot J_g$$

From the rate of production of entropy (6-b), one deduces then the volume dissipation  $\Phi$ , which should satisfy the fundamental inequality. It presents classically three contributions (7). The first one  $\Phi_1$  corresponds to the dissipative mechanisms related to plastic straining. The second one  $\Phi_2$  represents the thermal dissipation associated with heat transfer. The third one  $\Phi_3$  pertains to the diffusion dissipation linked to mass transport. It can be noted that the latter one is expressed as the product of the relative gas mass flux and the gradient of the difference between chemical potentials.

$$\Phi = \rho T \dot{s}_i = \Phi_1 + \Phi_2 + \Phi_3 \geq 0 \quad \Phi_1 = \sigma : \dot{\varepsilon}^p + \rho A \dot{p} + \rho X : \dot{\alpha} \quad \Phi_2 = -J_s \cdot \nabla T \quad \Phi_3 = -J_g \cdot \nabla [\Delta\mu] \quad (7)$$

### 3. CONSTITUTIVE LAWS

The following stage of modelling deals with the development of coupled constitutive equations.

#### 3.1. Thermodynamic potential - First set of constitutive equations

The thermodynamic formalism is based on the assumption of the existence of two potentials. The first one, namely the *thermodynamic potential*, corresponds here to the specific free energy of the mixture:  $\psi = u - Ts$ . The elastic behaviour being classically regarded as independent of the plastic one,  $\psi$  is split into elastic and inelastic parts, designated by  $\psi^e$  and  $\psi^p$  respectively.

We define first  $\psi^e$  as a scalar valued function of the elastic strain, the temperature and both mass fractions of gas and polymer, more precisely as follows:

$$\rho \psi^e = \sigma_o : \varepsilon^e - \rho s_o \Delta T + \rho \mu_g^o \Delta Y_g + \rho \mu_p^o \Delta Y_p + \frac{1}{2} \varepsilon^e : M : \varepsilon^e - \frac{\rho C}{2T_o} (\Delta T)^2$$

$$+ \frac{\rho D_g}{2} (\Delta Y_g)^2 + \frac{\rho D_p}{2} (\Delta Y_p)^2 - M_T : \varepsilon^e \Delta T - M_g : \varepsilon^e \Delta Y_g - M_p : \varepsilon^e \Delta Y_p$$

$$- d_g \Delta T \Delta Y_g - d_p \Delta T \Delta Y_p - d_{pg} \Delta Y_g \Delta Y_p \quad (8)$$

$$\Delta T = T - T_o \quad \Delta Y_g = Y_g - Y_g^o \quad \Delta Y_p = Y_p - Y_p^o \quad (9)$$

The initial value of any variable is identified by the superscript or subscript symbol 'o'. Note that there is no initial elastic strain.  $M$  denotes the fourth rank elastic stiffness tensor.  $C$  is the specific heat.  $D_g$  and  $D_p$  are linked to the diffusivity of the constituents of the mixture. Some coupling coefficients are

also introduced among which the tensors  $M_T$ ,  $M_g$  and  $M_p$  characterizing the dilation due to the variations of temperature, gas concentration and polymer concentration respectively.

Then  $\psi^p$  is classically expressed from a scalar valued function  $R$  pertaining to the isotropic hardening and a fourth-order tensor  $Z$  describing the kinematic hardening. These two terms depend here on the temperature and on each mass fraction, which results in the unusual form:

$$\psi^p(T, Y_g, Y_p, p, \alpha) = R(p, T, Y_g, Y_p) + \frac{1}{2} \alpha : Z(T, Y_g, Y_p) : \alpha \quad (10)$$

According to the generalized normality rule and the relation (2), the following set of constitutive equations is finally derived from this first potential (8-10):

$$\begin{aligned} \sigma = \sigma_0 + M : \varepsilon^e - M_T \Delta T - M_Y \Delta Y_g - \frac{B}{\rho} \left( \frac{\partial \rho}{\partial \varepsilon^e} \right)_{T, Y_i} + \frac{1}{2} \varepsilon^e : \left( \frac{\partial M}{\partial \varepsilon^e} \right)_{T, Y_i} : \varepsilon^e - \frac{\rho (\Delta T)^2}{2T_0} \left( \frac{\partial C}{\partial \varepsilon^e} \right)_{T, Y_i} \\ + (\Delta Y_g)^2 \left( \frac{\partial D}{\partial \varepsilon^e} \right)_{T, Y_i} - \Delta T \left( \frac{\partial M_T}{\partial \varepsilon^e} \right)_{T, Y_i} : \varepsilon^e - \Delta Y_g \left( \frac{\partial M_Y}{\partial \varepsilon^e} \right)_{T, Y_i} : \varepsilon^e - \Delta T \Delta Y_g \left( \frac{\partial d}{\partial \varepsilon^e} \right)_{T, Y_i} \end{aligned} \quad (11)$$

$$\begin{aligned} s = s_0 + \frac{C \Delta T}{T_0} + \frac{1}{\rho} M_T : \varepsilon^e + \frac{d \Delta Y_g}{\rho} - \left( \frac{\partial R}{\partial T} \right)_{p, Y_i} - \frac{1}{2} \alpha : \left( \frac{\partial Z}{\partial T} \right)_{Y_i} : \alpha + \frac{B}{\rho^2} \left( \frac{\partial \rho}{\partial T} \right)_{\varepsilon^e, Y_i} \\ - \frac{1}{2\rho} \varepsilon^e : \left( \frac{\partial M}{\partial T} \right)_{\varepsilon^e, Y_i} : \varepsilon^e + \frac{(\Delta T)^2}{2T_0} \left( \frac{\partial C}{\partial T} \right)_{\varepsilon^e, Y_i} - \frac{(\Delta Y_g)^2}{\rho} \left( \frac{\partial D}{\partial T} \right)_{\varepsilon^e, Y_i} \\ + \frac{\Delta T}{\rho} \left( \frac{\partial M_T}{\partial T} \right)_{\varepsilon^e, Y_i} : \varepsilon^e + \frac{\Delta Y_g}{\rho} \left( \frac{\partial M_Y}{\partial T} \right)_{\varepsilon^e, Y_i} : \varepsilon^e + \frac{\Delta T \Delta Y_g}{\rho} \left( \frac{\partial d}{\partial T} \right)_{\varepsilon^e, Y_i} \end{aligned} \quad (12)$$

$$\begin{aligned} \Delta \mu = \Delta \mu^0 + \frac{2D \Delta Y_g}{\rho} - \frac{1}{\rho} M_Y : \varepsilon^e - \frac{d \Delta T}{\rho} + \left( \frac{\partial R}{\partial Y_g} \right)_{T, p, Y_p} - \left( \frac{\partial R}{\partial Y_p} \right)_{T, p, Y_g} \\ + \frac{1}{2} \alpha : \left[ \left( \frac{\partial Z}{\partial Y_g} \right)_{T, Y_p} - \left( \frac{\partial Z}{\partial Y_p} \right)_{T, Y_g} \right] : \alpha - \frac{B}{\rho^2} \left[ \left( \frac{\partial \rho}{\partial Y_g} \right)_{\varepsilon^e, T, Y_p} - \left( \frac{\partial \rho}{\partial Y_p} \right)_{\varepsilon^e, T, Y_g} \right] \\ + \frac{1}{2\rho} \varepsilon^e : \left[ \left( \frac{\partial M}{\partial Y_g} \right)_{\varepsilon^e, T, Y_p} - \left( \frac{\partial M}{\partial Y_p} \right)_{\varepsilon^e, T, Y_g} \right] : \varepsilon^e - \frac{(\Delta T)^2}{2T_0} \left[ \left( \frac{\partial C}{\partial Y_g} \right)_{\varepsilon^e, T, Y_p} - \left( \frac{\partial C}{\partial Y_p} \right)_{\varepsilon^e, T, Y_g} \right] \\ + \frac{(\Delta Y_g)^2}{\rho} \left[ \left( \frac{\partial D}{\partial Y_g} \right)_{\varepsilon^e, T, Y_p} - \left( \frac{\partial D}{\partial Y_p} \right)_{\varepsilon^e, T, Y_g} \right] - \frac{\Delta T}{\rho} \left[ \left( \frac{\partial M_T}{\partial Y_g} \right)_{\varepsilon^e, T, Y_p} - \left( \frac{\partial M_T}{\partial Y_p} \right)_{\varepsilon^e, T, Y_g} \right] : \varepsilon^e \\ - \frac{\Delta Y_g}{\rho} \left[ \left( \frac{\partial M_Y}{\partial Y_g} \right)_{\varepsilon^e, T, Y_p} - \left( \frac{\partial M_Y}{\partial Y_p} \right)_{\varepsilon^e, T, Y_g} \right] : \varepsilon^e - \frac{\Delta T \Delta Y_g}{\rho} \left[ \left( \frac{\partial d}{\partial Y_g} \right)_{\varepsilon^e, T, Y_p} - \left( \frac{\partial d}{\partial Y_p} \right)_{\varepsilon^e, T, Y_g} \right] \end{aligned} \quad (13)$$

$$A = - \left( \frac{\partial R}{\partial p} \right)_{T, Y_i} \quad X = - Z : \alpha \quad (14)$$

$$B = \sigma_0 : \varepsilon^e + \frac{1}{2} \varepsilon^e : M : \varepsilon^e - \Delta T M_T : \varepsilon^e - \Delta Y_g M_Y : \varepsilon^e - d \Delta T \Delta Y_g + D (\Delta Y_g)^2 \quad (15)$$

$$D = \frac{\rho(D_g + D_p)}{2} + d_{pg} \quad M_Y = M_g - M_p \quad d = d_g - d_p \quad (16)$$

The four first terms defining the *stress tensor* (11) appear classically when one considers the direct effects of heat transfer and mass transport on mechanical problem, in other words when one takes account of both thermal and diffusion dilations. The other terms result from the indirect effect of elastic strain on material properties. As the elastic part of strain remains much smaller than the plastic one, they will be neglected in a first step. In the same way, the expression of the *specific entropy* (12) contains various terms due to the temperature dependence of material characteristics. The behaviour of polymers being deeply affected by thermal conditions, more particularly around its glass transition temperature, they are expected to modify strongly the entropy of the system. The third constitutive relation (13) characterizes the *difference between the chemical potential of gas and the one of polymer*. It presents some coupling terms whose identification and quantification will require probably the development of new experimental tests. Finally, the *thermodynamic forces associated with hardening variables* (14) are influenced by the temperature, as well as by both mass fractions via R and Z, which is physically motivated. Indeed, gas dissolution within the polymer matrix normally causes matrix plasticization, which acts on the mobility of polymer chains and facilitates their disentanglement [8]. Remark that  $(\partial/\partial)_*$  means partial derivative with \* constant.

### 3.2. Heat equation

The first principle (4), the Gibbs relation (5) and the above laws (11-14) yield a generalized heat equation, which offers four explanations for the local temperature evolution. The three first ones are classically taken into account: effects of heat flux and heat supply, effects tied to the rate of change of elastic strain and inelastic effects. The last contribution confirmed experimentally represents the heat generated by mass transport. It is directly related to the rate of variation of gas concentration. It will thus impact greatly on the field of temperatures during explosive decompression stages.

$$\begin{aligned} \rho C \dot{T} = & \{ -\text{div} J_T + r \} + \left\{ T \left[ \left( \frac{\partial \sigma}{\partial T} \right)_{\varepsilon^e, Y_i, p, \alpha} - \frac{\sigma}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_{\varepsilon^e, Y_i, p, \alpha} \right] : \dot{\varepsilon}^e \right\} \\ & + \left\{ \dot{\varepsilon}^p : \sigma - \rho \left[ T \left( \frac{\partial A}{\partial T} \right)_{\varepsilon^e, Y_i, p, \alpha} - A \right] \dot{p} - \rho \left[ T \left( \frac{\partial X}{\partial T} \right)_{\varepsilon^e, Y_i, p, \alpha} - X \right] : \dot{\alpha} \right\} \\ & + \left\{ \rho \left[ T \left( \frac{\partial(\Delta\mu)}{\partial T} \right)_{\varepsilon^e, Y_i, p, \alpha} - \Delta\mu \right] \dot{Y}_g \right\} \end{aligned} \quad (17)$$

### 3.3. Dissipation potential - Complementary constitutive equations

Let us now introduce the second potential, which is compatible a priori with the second law of thermodynamics (7), namely the *pseudo-potential of dissipation*, more exactly its dual form  $\delta^*$  obtained by Legendre-Fenchel transformation.

$$\begin{aligned} \delta^* = & F_I(\sigma, \rho A, \rho X, -\nabla T, -\nabla[\Delta\mu]) + \frac{1}{2} \nabla T \cdot [k_T \nabla T] \\ & + \frac{1}{2} \nabla(\Delta\mu) \cdot [k_\mu \nabla(\Delta\mu)] + \nabla T \cdot [c_{T\mu} \nabla(\Delta\mu)] \end{aligned} \quad (18)$$

$F_I$  designates the indicator function of the actual yield surface  $f$ . It depends not only on the stress tensor and the thermodynamic forces associated with internal variables but also on the gradient of temperature, as well as the gradient of difference between chemical potentials.  $k_T$ ,  $k_\mu$  and  $c_{T\mu}$  are the Onsager symmetric tensors. They vary with the state variables characterizing the system, as it is the case of all the other material characteristics. These three new coefficients define a part of the interrelations between thermal and diffusion processes. They have already been studied in the restricted mechanical framework of elasticity [9]. Note that this previous work underlined the key role played by  $k_\mu$  in the modelling of such coupling.

With the assumption of associated plasticity,  $\mathbf{n}$  the unit normal to the yield surface and  $\Lambda$  the plastic multiplier, the complementary laws deduced from this potential take the following form:

$$\dot{\boldsymbol{\varepsilon}}^p = \Lambda \mathbf{n} \quad \dot{\mathbf{p}} = \Lambda \left( \frac{\partial f}{\partial [\rho \mathbf{A}]} \right)_{\sigma, \rho \mathbf{X}, -\nabla T, -\nabla(\Delta\mu)} \quad \dot{\boldsymbol{\alpha}} = \Lambda \left( \frac{\partial f}{\partial [\rho \mathbf{X}]} \right)_{\sigma, \rho \mathbf{A}, -\nabla T, -\nabla(\Delta\mu)} \quad (19)$$

$$\mathbf{J}_s = \Lambda \left( \frac{\partial f}{\partial [-\nabla T]} \right)_{\sigma, \rho \mathbf{A}, \rho \mathbf{X}, -\nabla(\Delta\mu)} - k_T \nabla T - c_{T\mu} \nabla(\Delta\mu) \quad (20)$$

$$\mathbf{J}_g = \Lambda \left( \frac{\partial f}{\partial [-\nabla(\Delta\mu)]} \right)_{\sigma, \rho \mathbf{A}, \rho \mathbf{X}, -\nabla T} - k_\mu \nabla(\Delta\mu) - c_{T\mu} \nabla T \quad (22)$$

$\Lambda$  is then classically determined from the rate-independent consistency condition  $\dot{f} = 0$ . Considering the foregoing constitutive laws relative to internal variables (19-b, 19-c) and the relation (2) yields the below expression:

$$\Lambda = \frac{\mathbf{n} : \dot{\boldsymbol{\sigma}} - F_{\varepsilon^e} : \dot{\boldsymbol{\varepsilon}}^e - F_T \dot{T} - F_Y \dot{Y}_g - G_T \cdot \dot{\nabla} T - G_Y \cdot \dot{\nabla}(\Delta\mu)}{H} \quad (23)$$

$$H = \rho (Coef1)^2 \left( \frac{\partial^2 \mathbf{R}}{\partial \mathbf{p}^2} \right)_{T, Y_i} + \rho Coef2 : \mathbf{Z} : Coef2 \quad (24)$$

$$F_{\varepsilon^e} = [ Coef1 \left( \frac{\partial \mathbf{R}}{\partial \mathbf{p}} \right)_{T, Y_i} + Coef2 : \mathbf{Z} : \boldsymbol{\alpha} ] \left( \frac{\partial \rho}{\partial \boldsymbol{\varepsilon}^e} \right)_{T, Y_i} \quad (25)$$

$$F_T = \rho Coef1 \left( \frac{\partial^2 \mathbf{R}}{\partial T \partial \mathbf{p}} \right)_{Y_i} + \rho Coef2 : \left( \frac{\partial \mathbf{Z}}{\partial T} \right)_{Y_i} : \boldsymbol{\alpha} + [ Coef1 \left( \frac{\partial \mathbf{R}}{\partial \mathbf{p}} \right)_{T, Y_i} + Coef2 : \mathbf{Z} : \boldsymbol{\alpha} ] \left( \frac{\partial \rho}{\partial T} \right)_{\boldsymbol{\varepsilon}^e, Y_i} \quad (26)$$

$$F_Y = \rho \left[ \left( \frac{\partial^2 R}{\partial Y_g \partial p} \right)_{T, Y_p} - \left( \frac{\partial^2 R}{\partial Y_p \partial p} \right)_{T, Y_g} \right] Coef1 + \rho Coef2 : \left[ \left( \frac{\partial Z}{\partial Y_g} \right)_{T, Y_p} - \left( \frac{\partial Z}{\partial Y_p} \right)_{T, Y_g} \right] : \alpha$$

$$+ \left[ Coef1 \left( \frac{\partial R}{\partial p} \right)_{T, Y_i} + Coef2 : Z : \alpha \right] \left[ \left( \frac{\partial \rho}{\partial Y_g} \right)_{\varepsilon, T, Y_p}^e - \left( \frac{\partial \rho}{\partial Y_p} \right)_{\varepsilon, T, Y_g}^e \right] \quad (27)$$

$$G_T = \left( \frac{\partial f}{\partial [-\nabla T]} \right)_{\sigma, \rho A, \rho X, -\nabla(\Delta\mu)} \quad G_Y = \left( \frac{\partial f}{\partial [-\nabla(\Delta\mu)]} \right)_{\sigma, \rho A, \rho X, -\nabla T} \quad (28)$$

$$Coef1 = \left( \frac{\partial f}{\partial [\rho A]} \right)_{\sigma, \rho X, -\nabla T, -\nabla(\Delta\mu)} \quad Coef2 = \left( \frac{\partial f}{\partial [\rho X]} \right)_{\sigma, \rho A, -\nabla T, -\nabla(\Delta\mu)} \quad (29)$$

Involved coupling occurs via the plastic multiplier (23) in all the constitutive equations (19-22). The term denoted  $[F_{\varepsilon^e} : \dot{\varepsilon}^e]$  could probably be neglected in the case of slow evolution of elastic strain. The two following ones, identified by  $[F_T \dot{T}]$  and  $[F_Y \dot{Y}_g]$  respectively, are expected to influence strongly the plastic multiplier due to the significant temperature dependence of polymer behaviour for the first one and due to the rapid evolution of gas concentration during the explosive decompression process for the second one.

Some non-classical dependencies are introduced. For instance, the gradient of the difference between chemical potentials appears now in the expression of the yield surface, which results in a plastic flow dependent on the diffusion process but results also in a gas mass flux dependent on the plastic behaviour. Note that such an interaction between plasticity and mass transport has already been accepted from a physical viewpoint. Indeed, it is well known that in amorphous polymers, a strong link exists between spatial evolution of diffusion and distribution of stresses [10].

#### 4. CONCLUSION

A complete set of equations has been proposed in this paper with the aim of approaching the behaviour of polymers, in which several interacting processes, namely thermal, diffusion and mechanical phenomena, take place. It was detailed in the context of plasticity, which should offer interesting potential for the study of materials like semi-crystalline or glassy amorphous polymers during explosive decompressions. The main interest of such modelling lies in the fact that all these interactions have been considered in a framework as simple as possible. Several non-classical terms of coupling have been introduced, such as the gradients of temperature and chemical potentials in the hardening complementary laws. Some of them could certainly be neglected. The next step will concern the identification of the coupling terms and the evaluation of the ability of such modelling by confrontation with experiments. Numerical approaches and relative parametric studies will be made.

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