

## THE EFFECT OF CONFORMATIONAL RESTRICTIONS ON THE SEGMENTAL RELAXATION DYNAMICS OF SEMICRYSTALLINE POLYMERS

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**ABSTRACT.** A statistical mechanical model is used to describe the effect of restrictions, due to confinement by crystals, on the segmental relaxation dynamics of semicrystalline polymers. It is shown that the emergence of a rearrangement free energy barrier is intrinsically associated with the dynamic heterogeneity observable in relaxation experiments such as those from dielectric spectroscopy. The relaxation behaviour of a number of systems has been considered; the analysis shows that chain orientation has a significant effect on the degree of cooperativity. Moreover, the relaxation features appear to be influenced by the thermodynamic state of the embedding crystalline domains.

### 1. Introduction

Semicrystalline polymers are interesting model systems for investigating the effect of chain conformational constraints on the segmental dynamics in confined amorphous regions. Typical structures forming in these systems, consist of stacks of lamellar crystals separated by amorphous layers having a thickness ranging in the order of some nanometers [1].

The interest for this kind of systems is twofold. On the one hand, the process of confinement by crystals naturally drives the interlamellar amorphous regions towards a condition where the relaxation dynamics deviates significantly from that of an unconstrained melt. On the other, the thermodynamics of the embedding crystals is known to some extent [1, 2]; hence, the crystalline component can in fact be taken as a further probe for the characterisation of the amorphous relaxing component.

Apart of the above mentioned points concerning polymer dynamics, there are at least two well known features that generally apply to semicrystalline polymers and however, still lack of an even preliminary theoretical scheme for their understanding on thermodynamic grounds.

The first is that polymers never crystallize completely; there always remains a significant amorphous fraction which cannot convert into crystalline. Of course, this can be rather easily understood considering that chain entanglements and torsional defects - both preventing crystallization - remain trapped within the interlamellar amorphous regions,

due to chain connectivity and pinning to the crystal surfaces. However, this mechanistic description cannot offer a quantitative characterisation and, in this respect, its settlement within a structured theoretical framework would be desirable.

The second feature consists in that, when restrictions to conformational readjustments emerge, an increase of the average rigidity of the amorphous fraction is always accompanied by an enhancement of the dynamical heterogeneity. In isochronal, scanning temperature, low frequency mechanical experiments, this is shown by a progressive increase of both peak temperature and peak width of the  $\alpha$ -process upon crystallization. As an example, the case of poly(ethylene terephthalate) (PET) is reported in ref. [3]. On the other hand, isothermal measurements performed by means of broadband dielectric spectroscopy (BDS) reveal that the formation of crystals causes the progressive change of the dominant character of the  $\alpha$ -process. Namely, the fast and relatively narrow relaxation observed in very low crystallinity samples, converts into a significantly slower and broader process as crystallinity increases. Simultaneous X-ray diffraction and BDS measurements on poly(propylene adipate) and poly(propylene succinate) represent particularly clear examples of this phenomenology [4].

Recent work has been devoted to the development of a statistical mechanical mean-field model in terms of which the aspects considered above can be rationalised [5]. The model specifically deals with segmental conformational fluctuations within amorphous regions where confinement by crystals is more effective. Although some phenomenological aspects are still present in this approach, it represents a relevant attempt to relate segmental relaxation dynamics in confined amorphous regions with the thermodynamic state of the embedding crystal phase.

It is the aim of this contribution to summarize the important aspects of the above mentioned model and report supporting experimental evidence taken from the literature. In order to emphasize the conceptual aspects of the theory and to avoid redundancies with other papers, the model will not be described in detail. The reader is referred to ref. [5] for a thorough account of the constraint distribution function  $p(\zeta)$  (see below) and the procedure for extracting and fitting the relevant information from dielectric relaxation data.

## **2. Thermodynamic basis of a stationary relaxation behaviour under confinement regime**

The conformational relaxation in the amorphous regions of polymers are significantly influenced by confinement. As opposed to the collective character of segmental motion proper of wavelike perturbations, a localization of the dynamics within static cooperatively rearranging regions (SCRR) emerges in these conditions.

Chain connectivity and pinning at the boundaries of the confined regions represent constraints which affect the free energy  $F$  of the SCRRs ( $F$  would lower on dropping the constraints). The latter are quasi-isolated from the heat bath, in the sense that their conformational fluctuations are induced by the interaction with the heat bath via the coupling through the local degrees of freedom (e.g. the vibrational ones). Figure 1 shows a possible time evolution of  $F$  for a given SCRR. Successive minima correspond in general to different conformations (i.e. to different constraints to the evolution dynamics); each minimum can be abandoned - and a readjustment occurs - provided a suitable free energy fluctuation

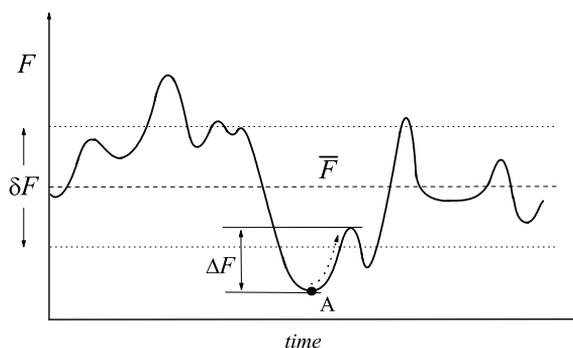


FIGURE 1. Schematic of the free energy time evolution pattern of a SCRR;  $\bar{F}$  and  $\delta F$  are the mean value of  $F$  and the dispersion respectively.

$\Delta F$ , which depends on the actual SCRR conformation too, is induced by the interaction with the heat bath. The lifetime  $\tau$  of a conformational state is thus connected to relatively faster local processes, having typical rates  $(\tau^*)^{-1}$ , by an Eyring-like relation:

$$\tau^{-1} \sim (\tau^*)^{-1} e^{-\Delta F/k_B T}, \quad (1)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature.

A free energy barrier  $\Delta F$  can be crossed (e.g. from point **A** in Fig. 1) provided a suitable *energy* fluctuation in the SCRR occurs. This can easily be shown by considering small deviations from equilibrium (local minimum of  $F$ ) at fixed volume; from ref. [6] sect. 21 indeed,

$$\Delta F = \Delta E - T\Delta S \simeq \frac{1}{2} \frac{\partial^2 E}{\partial S^2} (\Delta S)^2, \quad (2)$$

where  $\Delta S$  is the entropy change upon fluctuation (the relation  $T = \partial E/\partial S$  has been used).

Following the approach adopted by Adam and Gibbs for the description of liquids close to their glass transition [7], we extend this connection to the cases of comparatively large deviations from equilibrium by associating a reduced partition function

$$Z_{\zeta, n} \equiv \int_{\zeta}^{\infty} dE \rho_0 E^n e^{-E/k_B T} \quad (3)$$

to each of the  $z$  monomers forming a SCRR that is able to rearrange,  $n$  being a suitable integer (to be adjusted during data fitting below) and  $\rho_0$  a constant;  $\zeta$  is the energy threshold per monomer to be overcome in order that a fluctuation may induce a conformational change. As  $\zeta$  increases, so does the chemical potential of the mobile monomers

$$\Delta\mu(\zeta) \equiv -k_B T \ln \left( \frac{Z_{\zeta}}{Z_0} \right) \equiv \Delta F(\zeta)/z. \quad (4)$$

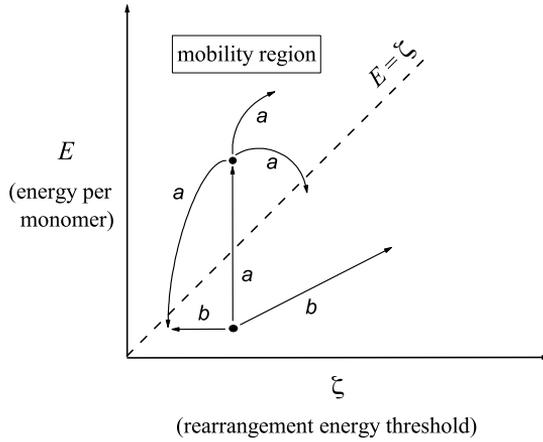


FIGURE 2. Schematic of an energy plot where possible (a) and prohibited (b) paths are shown. The  $E = \zeta$  line separates the mobility region ( $E \geq \zeta$ ) from that where monomers are in SCRRs with frozen conformations.

Only those monomers which happen to have an energy larger than  $\zeta$ , belong to SCRRs which may undergo a conformational readjustment leading in general to a further change of  $\zeta$ . In an energy plot such as that depicted in Fig. 2 this is to say that paths like those labelled with an "a" are allowed, while those labelled with a "b" are not.

In a system where crystallization has come to completion, the whole amorphous component consists of a stationary distribution  $p(\zeta)$  of monomers. We consider the set of all monomers with energy larger than  $\zeta$  (i.e. the mobile ones) as a thermodynamic subsystem in thermal equilibrium with the environment; its volume is not allowed to fluctuate. Note that, in general, the conformational space explored by a given SCRR may not span all possible values of  $\zeta$ . Hence, our hypothesis of thermal equilibrium consists in assuming that the number of SCRRs in which the whole amorphous component is partitioned is enormously large and the variety of different local conformational spaces densely explored; each local constraining condition due to the crystals then may adjust following our global thermodynamic criterion.

The equilibrium condition is established by extremizing the quantity (referred to a monomer)

$$A \equiv U[p(\zeta)] + k_B T \int_0^\infty p(\zeta) \ln p(\zeta) d\zeta + \lambda \overline{\Delta\mu}[p(\zeta)], \tag{5}$$

where the functional  $U[p(\zeta)]$  is the mean energy of all mobility states ( $E \geq \zeta$ ) that can be generated by fluctuation from SCRRs of virtually frozen conformations (i.e. given  $\zeta$ ),  $\lambda$  is a Lagrange multiplier and

$$\overline{\Delta\mu}[p(\zeta)] \equiv \int_0^\infty d\zeta p(\zeta) \Delta\mu(\zeta) \tag{6}$$

is the mean chemical potential of the whole population of mobile monomers. The latter must be a constant in a steady state and, as shown below, is in fact the link to the thermodynamic state of the crystalline phase.

As a result of the extremization procedure we find [5]

$$p(\zeta) = N(\lambda, n) e^{-w_r(\zeta)\langle E \rangle_\zeta / k_B T - \lambda \Delta\mu(\zeta)}, \quad (7)$$

where  $N(\lambda, n)$  is a normalization factor,

$$\langle E \rangle_\zeta = -\frac{\partial}{\partial(k_B T)^{-1}} \ln Z_\zeta \quad (8)$$

and

$$w(\zeta) \equiv Z_\zeta / Z_0 \quad (9)$$

is the probability that a monomer with energy threshold  $\zeta$  undergoes a fluctuation to a state with energy larger than  $\zeta$  (being  $Z_0 \equiv Z_\zeta|_{\zeta=0}$ ).

Once the distribution  $p(\zeta)$  is known, the conformational relaxation function  $\phi(t)$  can be expressed as a superposition of Debye relaxations in the form

$$\phi(t) = \int_0^\infty d\zeta p(\zeta) \exp\left\{-\frac{t}{\tau^*} e^{-z \Delta\mu(\zeta)/k_B T}\right\}; \quad (10)$$

it is in fact this model function which will be fitted to the experimental data, thus allowing to extract information about  $z$ ,  $\overline{\Delta\mu}$ , and the dispersion

$$\delta[\Delta\mu] \equiv \sqrt{-\frac{\partial \overline{\Delta\mu}}{\partial \lambda}}. \quad (11)$$

### 3. Application to the analysis of literature data concerning dielectric relaxation

BDS measurements performed on semicrystalline polymers offer an interesting opportunity to apply the model function  $\phi(t)$ , eq. 10, in order to extract information on cooperativity and thermodynamic state (i.e.  $z$  and  $\overline{\Delta\mu}$  respectively) of the confined amorphous regions.

The treatment of the  $\varepsilon \equiv \varepsilon(\omega)$  data (where  $\varepsilon$  and  $\omega$  are the complex dielectric permittivity and the angular frequency respectively) is not trivial and the interested reader may find exhaustive details, also with regards to the fitting procedures, in ref. [5]. What is worth pointing out is that the information we are interested in, is contained in the temperature  $T_{meas}$  of the measurement and in the parameters  $\tau_\alpha$  and  $a_\alpha$  associated to the Havriliak-Negami representation of the relevant segmental relaxation contribution, i.e.

$$\varepsilon_\alpha(\omega) \sim \frac{1}{[1 + (i\omega\tau_\alpha)^{a_\alpha}]^{b_\alpha}}. \quad (12)$$

In the last equation,  $\tau_\alpha$  is the central relaxation time and  $a_\alpha \in ]0, 1]$  is the width parameter (for a Debye process, the narrowest,  $a_\alpha = 1$ ). The parameter  $b_\alpha (\in ]0, 1])$  describes the asymmetry of the process; however, in the majority of cases, and in particular those to be considered below, crystal confinement symmetrizes the relaxation profile; hence,  $b_\alpha = 1$  will always be assumed in the following.

Once the relevant parameters are known, the correlation function associated to eq. 12 can be derived by a Fourier cosine transform [8] and finally the  $\phi(t)$  function of eq. 10 is fitted to it. The results of this analysis are reported in Table 1.

We first note the significant dependence of cooperativity on the mean chain orientation. Indeed, oriented PET and PEN exhibit larger  $z$  values than the corresponding isotropic materials (see Table 1). Understanding this effect requires the use of detailed models for the description of chain statistics. However, previous investigations on PET based on a gaussian chain model [3], suggest that this could be due to an enhancement of the density autocorrelation length along the mean chain direction (see also ref. [5]).

Another point to consider is that  $\tau^* \ll \tau_\alpha$  is always found, which of course supports the picture that has been outlined above (cf. eq. 1 and the considerations just preceding).

With regards to the chemical potential, the approximate relation

$$\delta[\Delta\mu] \approx \overline{\Delta\mu} \quad (13)$$

always holds. Technically, this follows from the quasi-poissonian character of the distribution  $p(\zeta)$  of eq. 7 with respect to  $\Delta\mu(\zeta)$ . However, from the physical point of view, this means that the SCRRs behave like thermodynamically small subsystems. It is known in fact that as the size of a subsystem decreases, the fluctuation amplitude of an extensive quantity which is allowed to vary, approaches the corresponding mean value. In the present case, the extensive quantity is the free energy  $\Delta F = z \overline{\Delta\mu}$ , and  $z$  is indeed found to be small.

Considering the connection with the thermodynamic state of the crystals, the chemical potential change associated to the transition of a monomer from the liquid state (in an undercooled and unconstrained melt) to the crystalline state can be estimated by means of the parameters reported in Table 1 using the approximate formula

$$\Delta\mu_{cryst}(T) \simeq \frac{H_f(T - T_m)}{T_m} \frac{T}{T_m} \quad (14)$$

due to Hoffman [13, 14], where  $H_f$  is the enthalpy of fusion and  $T_m$  is the equilibrium melting point. This quantity has been calculated for the different systems at their crystallization temperature value  $T_c$  (see Table 1); the absolute values of  $\Delta\mu_{cryst}$  are then correlated with the worked out values of  $\overline{\Delta\mu}$  in Fig. 3.

The message from Fig. 3 is clear: The progressive introduction of conformational constraints in the amorphous component, due to crystal growth, increases its chemical potential ( $\overline{\Delta\mu} > 0$ ); this mechanism remains active until further crystallization causes  $\overline{\Delta\mu}$  to become so large that it cannot be balanced by  $\Delta\mu_{cryst} (< 0)$  and the overall chemical potential change associated to a crystallization event (i.e. the average over both a crystallizing monomer and e.g. the adjoining one along the chain, but still in the amorphous domain) reaches a stationary value.

#### 4. Concluding remarks

The limited number of cases considered so far does not allow to draw general conclusions about the interplay between the crystalline and the amorphous components in semicrystalline polymers. Nevertheless, the analysis points out new peculiar aspects of polymer crystallization and confined relaxation in general.

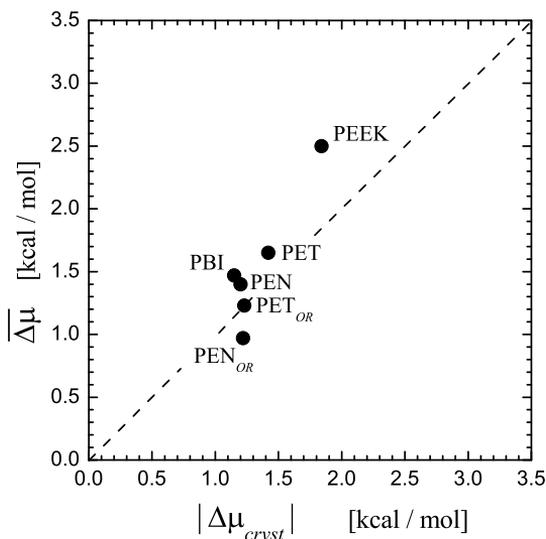


FIGURE 3. Correlation of the average chemical potential increase  $\overline{\Delta\mu}$  (associated to the gain of mobility) due to the effect of conformational constraints, with the chemical potential drop  $|\Delta\mu_{cryst}|$  associated to the transition from the undercooled, unconstrained liquid state to the crystalline state at  $T_c \simeq T_{meas}$ .

The fact that only limited crystallinity fractions can be reached in polymers, certainly has to be related to defects (chain torsions or entanglements) which cannot escape from the amorphous domains, due to chain connectivity. Undoubtedly, the density of these defects increases during crystallization and this process manifests through the relaxation properties of the confined amorphous regions. The analysis proposed in the preceding sections allows in fact to extract information about the thermodynamic state of these domains (i.e.  $\overline{\Delta\mu}$ ) through the measure of their dynamic heterogeneity (i.e.  $\delta[\Delta\mu]$ ); eq. 13 is central to this point, representing an intrinsic connection between two apparently independent quantities.

Regarding the influence of the thermodynamic state of the crystals on the relaxation properties of the amorphous domains, Fig. 3 strongly suggests that in fact the relaxation features carry information about the crystalline embedding phase. The same figure also suggests that the approximate relationship

$$\overline{\Delta\mu} \approx -\Delta\mu_{cryst} \quad (15)$$

could be the manifestation of an underlying thermodynamic balance condition.

Although the results presented in this work are far from being definitive, we hope that they will be stimulating hints for further research in this field.

Sample	$H_f$ (kcal/mol)	$T_m$ (°C)	$T_c$ (°C)	$T_{meas}$ (°C)	$a_\alpha$	$\tau_\alpha$ (sec)	$\tau^*$ (sec)	$z$	$\Delta\mu$ (kcal/mol)	$\delta[\Delta\mu]$ (kcal/mol)
PBI [9]	6.6	156	60	60	0.4	$2 \times 10^{-5}$	$4 \times 10^{-7}$	2.7	1.47	0.89
PET [5]	6.4	285	96	96	0.4	$5 \times 10^{-3}$	$2 \times 10^{-5}$	2.5	1.65	1
PET <sub>OR</sub> [5]	6.4	285	140	130	0.18	$4.2 \times 10^{-3}$	$5.4 \times 10^{-8}$	7.6	1.23	0.88
PEN [10]	5.95	337	165	155	0.26	$3.2 \times 10^{-4}$	$1.2 \times 10^{-7}$	6.2	1.4	0.85
PEN <sub>OR</sub> [11]	5.95	337	160	155	0.2	$10^{-3}$	$1.9 \times 10^{-9}$	11.2	0.97	0.59
PEEK [12]	8.9	395	200	186	0.33	$8 \times 10^{-7}$	$1.5 \times 10^{-11}$	4.2	2.5	0.97

TABLE 1. Melting enthalpy  $H_f$ , melting temperature  $T_m$ , crystallization temperature  $T_c$ , measurement temperature  $T_{meas}$ , width parameter  $a_\alpha$ , central relaxation time  $\tau_\alpha$ , relaxation function parameters  $\tau^*$  and  $z$ , average chemical potential  $\Delta\mu$  and its dispersion  $\delta[\Delta\mu]$ , for the different polymer species considered: poly(butylene isophthalate) (PBI), poly(ethylene terephthalate) crystallized from either an isotropic or an oriented glass (PET and PET<sub>OR</sub> respectively), poly(ethylene-2, 6-naphthalate) crystallized from an isotropic glass (PEN) or uniaxially oriented at  $T = 160^\circ\text{C}$  (PEN<sub>OR</sub>) and poly(ether ether ketone) (PEEK) crystallized from an isotropic glass. The references from which the dielectric relaxation data have been drawn are explicitly indicated in the first column, next to the acronyms of the species;  $H_f$  and  $T_m$  can be found in several handbooks or, e.g. in the ATHAS data bank.

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