

Correlation between temperature–pressure dependence of the α -relaxation and configurational entropy for a glass-forming polymer

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Available online 26 July 2005

Abstract

In this work we investigated the temperature–pressure dependence of the relaxation time of the α -relaxation process of poly(vinyl acetate) (PVAc). By means of dielectric spectroscopy technique the relaxation time of the α -process was measured over a broad range of frequencies (10^{-1} – 10^7 Hz), pressures (0–300 MPa) and temperatures (320–460 K). Two different approaches were used to analyze the temperature–pressure dependence of the relaxation time: the phenomenological Vogel–Fulcher–Tammann (VFT) equation and the pressure extended Adam–Gibbs (PEAG) equation recently proposed. We compared both results and discussed the validity of the VFT approach for PVAc at different pressures. We found an excellent agreement between the experimental data and the PEAG equation, which only needs four parameters to describe the complete temperature–pressure dependence of the relaxation time of the α -process. Finally, we showed that the thermal and volumetric contributions to the configurational entropy are clearly separated for PVAc.

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PACS: 64.70.Pf; 77.22.Gm; 65.60.+a

1. Introduction

By cooling at sufficiently high rates many liquids do not crystallize, becoming supercooled and finally enter to the glassy state where the molecular motions of the system are *frozen* in the time scale of the experiment. Although the most common way to reach the glassy state is by decreasing the temperature of the system, the glass transition can also be approached by applying high enough pressure to a supercooled liquid. Both

the increase of pressure and the decrease of temperature result in slower molecular motions. These two different ways of approaching the glass transition allow to separate thermal and volumetric effects and to reach a better understanding of the glass transition process.

The temperature dependence of the relaxation time of a supercooled liquid is usually described by the Vogel–Fulcher–Tammann (VFT) [1–3] empirical equation given by $\tau(T) = \tau_0 \exp(DT_0/(T - T_0))$. Although the VFT dependence of the relaxation time with temperature is, in general, in good agreement with the experimental data, the lack of any clear physical interpretation does not help in the understanding of the nature of the glass transition. However, it has been shown [4] that the temperature dependence of the relaxation time expressed by the VFT equation can be

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derived, under certain assumptions, from the Adam–Gibbs (AG) theory [5] which is based on the concept of the configurational entropy and allows linking the dynamic and thermodynamic behaviour of the glass formers.

Additionally, the effect of pressure variation on the dynamics of the α -relaxation process can be very useful to investigate both thermal and density effects. Some of the seminal works in this area were done in the sixties [6–8] and a renewed interest has arisen during the last years [9–13]. The improvement of the experimental techniques has made possible to obtain a large amount of accurate data over broader ranges of pressure, temperature and frequency and therefore contributes to the better understanding of the involved processes. Thus, a new equation describing the behaviour of the structural relaxation time, $\tau(T, P)$, as a function of both pressure and temperature, has been recently proposed [10]. This equation was derived from the Adam–Gibbs (AG) theory by writing the configurational entropy, S_c , in terms of the excess of both thermal heat capacity and thermal expansion.

In this work the α -relaxation of poly(vinyl acetate) (PVAc) was studied using dielectric spectroscopy (10^{-1} – 10^7 Hz) over a temperature range between 320 and 460 K and pressures up to 300 MPa. The temperature–pressure dependence of the experimental α -relaxation times was found to be very well described using an extended AG equation [10] with thermal and expansion coefficients determined from calorimetric and PVT data respectively.

2. Theory

The AG theory, which is based on the assumption of cooperatively rearranging regions, gives an expression that relates the relaxation time with the configurational entropy (S_c) [5]

$$\tau = \tau_0 \exp\left(\frac{C}{TS_c}\right), \quad (1)$$

where C is a material constant and S_c is the configurational entropy. However, since S_c is not accessible experimentally, it is usually identified with the excess entropy ($S_{ex} = S_{melt} - S_{crystal}$). Although there is still an open debate about this point, some findings seem to suggest a general validity of the proportionality between S_{ex} and S_c [14]; under this assumption we identify S_c with S_{ex} and therefore the proportionality constant between them will only affect the value of C in Eq. (1). Thus S_c can be estimated as [4]

$$S_c(T) = \frac{\Delta H_{melt}}{T_{melt}} - \int_T^{T_{melt}} \frac{\Delta C_P(T')}{T'} dT', \quad (2a)$$

where $\Delta C_P = C_P^{melt} - C_P^{crystal}$ would be the excess heat capacity. In many polymers no melt is observed and a different procedure has to be followed to calculate S_c . Usually $C_P^{crystal}$ is identified with C_P^{glass} and in order to access the excess entropy what is calculated is

$$S_c(T) = \int_{T_K}^T \frac{\Delta C_P(T')}{T'} dT', \quad (2b)$$

where $\Delta C_P = C_P^{melt} - C_P^{glass}$ and T_K is the Kauzmann temperature, which used to be of the order of $T_g - 50$ K, where the excess entropy would vanish. Generally, an inverse temperature dependence is assumed for ΔC_P ($\Delta C_P = K/T$) and therefore, by integrating equation (2b) and replacing S_c in Eq. (1), with $T_0 = T_K$, the VFT expression for the temperature dependence of the relaxation time is recovered. However, as we will see in this work, this temperature dependence for ΔC_P is not always valid.

Recently, Casalini et al. [10] have proposed an extension of the Eq. (2) for the configurational entropy (S_c) which also includes pressure as an independent variable by adding a term related to the pressure change. Thus, the temperature and pressure dependence of the S_c is given by

$$S_c(T, P) = g_T(P) \int_{T_K}^T \frac{\Delta C_P(T')}{T'} dT' - g_P(T) \times \int_0^P \Delta \left(\frac{\partial V}{\partial T} \right)_{P'} dP', \quad (3)$$

where

$$\Delta \left(\frac{\partial V}{\partial T} \right)_P = \Delta \left(\frac{\partial V}{\partial T} \right)_P^{melt} - \Delta \left(\frac{\partial V}{\partial T} \right)_P^{glass} \quad (4)$$

is the difference of the thermal expansivity of the melt and the glass; g_T and g_P are factors which could eventually depend on pressure and temperature, respectively. If they are constant then the thermal and volumetric contributions to the configurational entropy are very well separated and their relative weights can be estimated. In addition, if ΔC_P follows a K/T law and g_P/g_T does not depend on temperature a VFT behaviour is recovered at any arbitrary fixed pressure with unique set of values for τ_0 and D . In this case we obtain the pressure extended AG equation [11]

$$\tau(T, P) = \tau_0 \exp\left(\frac{DT_0^*}{T - T_0^*}\right), \quad (5)$$

$$T_0^*(P) = \frac{T_K}{1 - \frac{g_P}{g_T} \frac{1}{S_\infty} \int_0^P \Delta \left(\frac{\partial V}{\partial T} \right)_{P'} dP'}, \quad (6)$$

where τ_0 , D and T_K are the VFT parameters at atmospheric pressure, and S_∞ is the excess entropy at very high temperature and atmospheric pressure.

3. Experimental

3.1. Samples

Poly(vinyl acetate) (PVAc) ($M_w = 93080$ g/mol) was used for this study. The calorimetric glass transition temperature, T_g , was determined by differential scanning calorimetry (DSC). The inflection point of the C_p versus temperature curve was 34.8 ± 0.1 °C.

3.2. Dielectric measurements under pressure

Dielectric measurements were carried out in a pressure cell (0–300 MPa) supplied by Novocontrol GmbH. The range 10^{-1} – 10^5 Hz was measured with an EGG5302 lock-in amplifier in combination with a Chelsea dielectric interface whereas for the range 10^3 – 10^7 Hz a HP4192LF impedance analyzer was used. A full description of the experimental techniques can be found in reference [13]. The sample measurements were performed by frequency sweeps at constant temperature, with stability better than ± 0.1 K, and constant pressure, with stability better than ± 2 MPa.

4. Results and discussion

4.1. Dielectric relaxation spectra and relaxation times

Fig. 1a shows the dielectric loss (ϵ''), as a function of frequency, under atmospheric pressure, at different temperatures as determined using the pressure cell. Isothermal spectra, at various pressures, are shown in Fig. 1b. The central part of the main peak (i.e. the α -relaxation) was described using the Alvarez–Alegría–Colmenero function [15], which is a particular case of the Havriliak–Negami (HN) function

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{[1 + (i\omega\tau_{\text{HN}})^\alpha]^\beta}, \quad (7)$$

where $\Delta\epsilon$ is the relaxation strength, τ_{HN} is the relaxation time and α and β are shape parameters with $\beta = 1 - 0.812(1 - \alpha)^{0.387}$. This last constraint allows reducing the number of free parameters (without significant decrease of the fitting quality) and also deducing from this frequency domain fit the parameters of the corresponding time domain Kohlrausch–Williams–Watts (KWW) function [15].

Fig. 2 shows the Arrhenius plot for the relaxation time of maximal loss $\tau = \tau_{\text{max}} (= \tau_{\text{HN}}(\sin(\alpha\pi/(2 + 2\beta)))^{-1/\beta} (\sin(\alpha\beta\pi/(2 + 2\beta)))^{1/\beta})$ [16] at different pressures. Filled and dashed lines represent fits to the phenomenological and theoretical predictions as explained below. The experimental data are in very good agreement with those previously published by O'Reilly [6] and by Heinrich and Stoll [17].

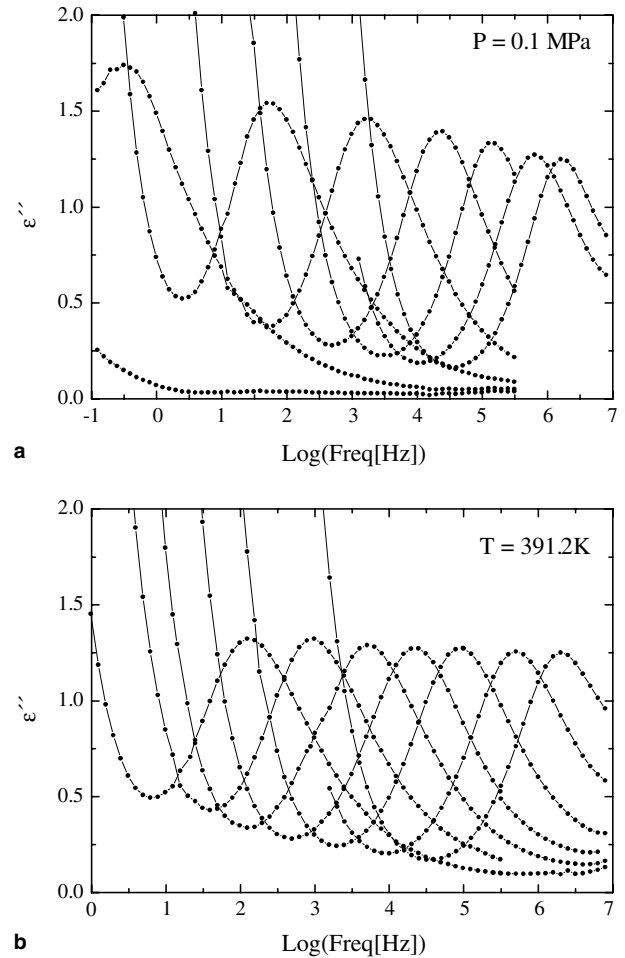


Fig. 1. (a) Dielectric loss (ϵ'') at atmospheric pressure and different temperatures (from left to right: 300.5, 313.5, 326.4, 339.4, 352.3, 365.3, 378.3 and 391.2 [K]). (b) Dielectric loss (ϵ'') at 391.2 K and different pressures (from left to right: 300, 250, 200, 150, 100, 50 and ≈ 0 MPa).

4.2. Phenomenological approach

Since the VFT equation has shown to be very useful for an empirical description of the temperature dependence of the relaxation times for several glass formers, it is reasonable to use it as a first approximation. Actually, some expressions, which are ‘natural’ extensions of the VFT equation, have been recently proposed [9, 18–20] to describe the temperature–pressure dependence of the relaxation times. Phenomenological expressions like

$$\tau(T, P) = \tau_0 \exp\left(\frac{D(T_0 + bP + cP^2)}{T - (T_0 + bP + cP^2)}\right), \quad (8)$$

which is a particular case of Eq. (5), were found very useful to fit the temperature–pressure dependence of the relaxation time of several glass formers [11,21]. However, by keeping τ_0 and D those determined from atmospheric pressure, it is not possible to describe prop-

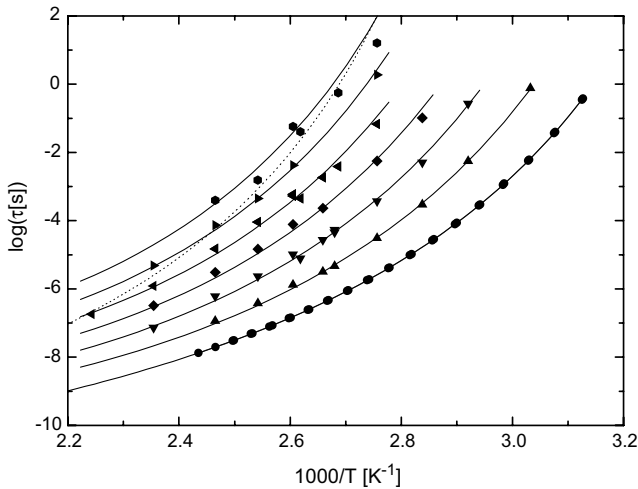


Fig. 2. Relaxation time of the α -process of PVAc as a function of inverse temperature at different pressures (from top to bottom: 300, 250, 200, 150, 100, 50 MPa, atmospheric pressure ($\cong 0$ MPa)). Dashed line corresponds to Eq. (8) with $P = 300$ MPa and τ_0 and D those determined from atmospheric pressure; the experimental data at $P = 0$ MPa were fitted with both Eq. (10) and the VFT function (both curves are overlapped in the figure); filled lines represent the predicted values (see text) according to Eq. (13) (note that for $P = 0$ MPa Eq. (13) reduces to Eq. (10)).

erly the experimental data for PVAc by means of Eq. (8) as shown in Fig. 2 for $P = 300$ MPa (dashed line). If we leave τ_0 as a free parameter, although the fitting is good, τ_0 varies more than one order of magnitude between atmospheric pressure and 300 MPa which seems to be unrealistic to our understanding. A possible explanation for this atypical behaviour of PVAc could be related with the strong decrease of ΔC_p with temperature as reported in the literature [22] and shown in Fig. 3. As

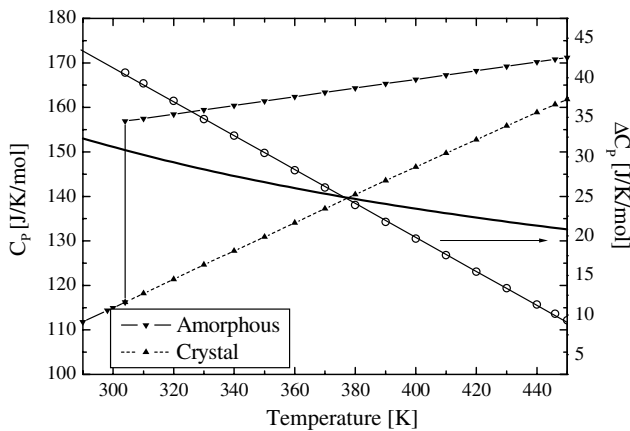


Fig. 3. Heat capacity (C_p) for both melt and crystal (taken from Ref. [22]), and excess heat capacity ($\Delta C_p = C_p^{\text{melt}} - C_p^{\text{crystal}}$) as a function of temperature. The dashed line (with non-inverted triangles) represents the extrapolated values of C_p^{crystal} to temperatures above the glass transition. The values of ΔC_p (open circles) decrease linearly with temperature as shown by the linear fit to the data. The thick line represents the best fit of the ΔC_p data to equation $\Delta C_p = K/T$.

aforementioned, what is generally assumed is that the temperature dependence of ΔC_p should be not far from $\Delta C_p = K/T$ which yield the VFT equation in the AG framework. However, as shown in Fig. 3 the PVAc temperature dependence of ΔC_p is actually much stronger than the K/T , which means that by using AG the VFT equation is not recovered. As it was shown above, even if the VFT is valid to fit the data at any fixed pressure, a complete temperature–pressure description for the relaxation time is not possible by using extensions of the VFT equation like Eq. (8).

Taking all these features into account we have checked whether the extended Adam–Gibbs frame, namely Eq. (3) in combination with Eq. (1), can provide a full description of the temperature–pressure dependence of the relaxation time.

Heat capacity and thermal effects. Fig. 3 shows the heat capacity (C_p) and the excess heat capacity (ΔC_p) for the PVAc in the temperature range of interest. It is clear from this figure that ΔC_p decreases in a nearly linear fashion with temperature according to the empirical equation $\Delta C_p = b - mT$, where $b = (103.96 \pm 0.02)$ $\text{JK}^{-1} \text{mol}^{-1}$ and $m = (0.21 \pm 0.01)$ $\text{JK}^{-2} \text{mol}^{-1}$. According with this, the thermal contribution to the configurational entropy would be

$$S_c(T, P \cong 0) = g_T \int_{T_K}^T \frac{\Delta C_p(T')}{T'} dT' = g_T (b \ln(T/T_K) - m(T - T_K)). \quad (9)$$

Thus, by introducing this result in Eq. (1), the temperature dependence of the relaxation time at atmospheric pressure would be given by

$$\tau(T, P \cong 0) = \tau_0 \exp \left[\frac{C/g_T}{T(b \ln(T/T_K) - m(T - T_K))} \right]. \quad (10)$$

By using Eq. (10) to fit the experimental data we got $\log(\tau_0[\text{s}]) = -14.1 \pm 0.1$, $C/g_T = (99041 \pm 540)$ J mol^{-1} and $T_K = 255.5 \pm 0.2$ K.

It is interesting to note that even when the VFT equation is not recovered from the AG theory, it is still valid as a phenomenological description of the experimental data. Fig. 2 shows the best fit to the experimental data (at atmospheric pressure) by using both Eq. (10) and VFT equation with $\log(\tau_0[\text{s}]) = -12.8 \pm 0.1$, $D = 6.6 \pm 0.1$ and $T_0 = 259.8 \pm 0.1$ K. The difference between both curves is less than the width of the line and therefore they are superimposed in the figure.

Thermal expansion and volumetric effects. In order to calculate the volumetric contribution to the configurational entropy we need to estimate $\Delta(\partial V/\partial T)_p$. The temperature dependence of the volume was estimated by plotting the specific volume for PVAc, as given in reference [23], versus temperature and taking the slopes below and above T_g . For the different pressures the Tait

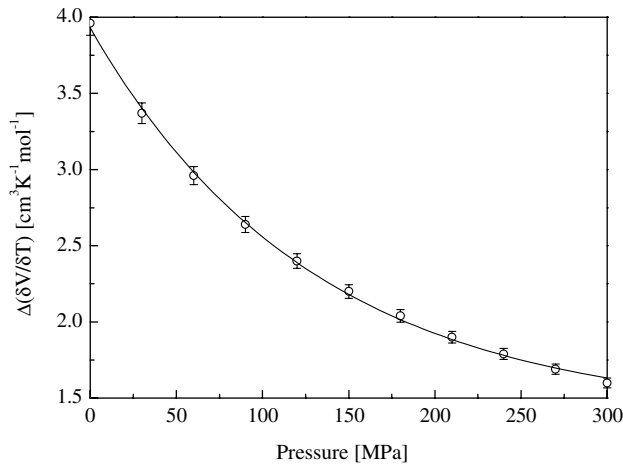


Fig. 4. $\Delta(\partial V/\partial T)_P$ as a function of pressure. The data were fitted with an empirical exponential function (see text).

equation [23] was used with the parameters reported in [24] for the glassy state. Fig. 4 shows the pressure dependence of $\Delta(\partial V/\partial T)_P$ so obtained and the best fit to an empirical exponential decay according to

$$\Delta(\partial V/\partial T)_P = \Delta(\partial V/\partial T)_{P=0} - A[1 - \exp(-P/P_0)] \quad (11)$$

with $A = (2.15 \pm 0.03)10^{-2} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$, $P_0 = (129 \pm 5) \text{ MPa}$ and $\Delta(\partial V/\partial T)_{P=0} = (3.35 \pm 0.03)10^{-2} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$. Therefore the pressure contribution to the configurational entropy is

$$g_P \int_0^P \Delta(\partial V/\partial T)_{P'} dP' = g_P P_0 \left[\Delta(\partial V/\partial T)_{P=0} \frac{P}{P_0} - A \left[\frac{P}{P_0} + \exp(-P/P_0) - 1 \right] \right]. \quad (12)$$

By using Eqs. (9) and (12) in Eq. (3) and then by replacing in Eq. (1) we have the following expression for the temperature–pressure dependence of the relaxation time

$$\tau(T, P) = \tau_0 \exp \left[\frac{C/g_T}{T \left\{ \left[b \ln \left(\frac{T}{T_K} \right) - m(T - T_K) \right] - \frac{g_P}{g_T} P_0 \left[\Delta(\partial V/\partial T)_{P=0} \frac{P}{P_0} - A \left(\frac{P}{P_0} + \exp(-P/P_0) - 1 \right) \right] \right\}} \right]. \quad (13)$$

Since we already know the values of $\log(\tau_0)$, C/g_T and T_K , (determined from the fitting at atmospheric pressure) we can use the experimental values of the relaxation time to estimate g_P/g_T for different temperatures and pressures. Fig. 5 shows g_P/g_T values versus temperature for different pressures; no clear temperature or pressure dependence is observed besides the experimental uncertainties. Given that the effect of pressure is

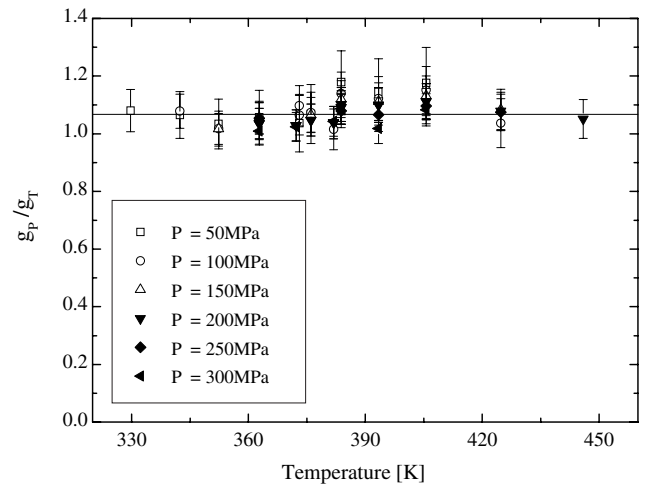


Fig. 5. Coefficient g_P/g_T as a function of temperature at different pressures. Open symbols represent low pressure data whereas full symbols are used for high pressure data. The line represents the estimated constant weighted value (see text).

more significant at high pressures, we estimated an average value by weighting the data with the corresponding pressure values. The solid line in Fig. 5 represents this weighted average for all values. This is an important result which shows that the temperature and pressure contributions to the configurational entropy come exclusively from the respective integrals in Eq. (3).

Once the value of g_P/g_T is known we can use Eq. (13), with the parameters previously estimated at atmospheric pressure ($\log(\tau_0)$, C/g_T and T_K), to calculate the relaxation time at any temperature and pressure. Fig. 2 shows the excellent agreement among experimental data and the predicted values (filled lines) for the relaxation time using Eq. (13).

5. Conclusions

We have shown that even if the phenomenological VFT equation gives an excellent description of the tem-

perature dependence of the relaxation time at any given fixed pressure, the complete description of the temperature–pressure dependence is not possible by keeping τ_0 constant. By leaving τ_0 as a free parameter we got an unreasonable change of τ_0 with pressure.

The fit of experimental data with Eq. (13) shows not only the validity of the AG frame but also that it is a more general theory which includes the VFT behaviour

as a particular case. It is important to note that in addition to the thermodynamic data taken from the literature, only four parameters are needed to fit τ (T, P): $\log(\tau_0)$, C/g_T and T_K (from $P = 0$ MPa data) and g_P/g_T .

The fact that the value of g_P/g_T is constant is an indication that thermal and volumetric contributions to the configurational entropy for PVAc are well separated and their values are given by the integrals expressions in Eq. (3).

Acknowledgements

This work has been supported in part by the Spanish Ministry of Science and Technology (MICyT) (Project MAT 2001/0070) and by the Government of the Basque Country (Project 9/UPV 00206.215-13568/2001).

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