Methyl group dynamics in a confined glass

A.J. Moreno¹, J. Colmenero², ³, ⁴, A. Alegría², ³, C. Alba-Simionesco⁵, G. Dosseh⁵, D. Morineau⁵, ⁶, B. Frick⁷

¹ Laboratoire des Verres, CNRS-UMR 5587, Université de Montpellier II, Bâtiment 13, F-34095 Montpellier (France).
² Dpto. Física de Materiales UPV/EHU, Apdo. 1072, E-20080 San Sebastián (Spain).
³ Unidad de Física de Materiales (CSIC-UPV/EHU), Apdo. 1072, E-20080 San Sebastián (Spain).
⁴ Donostia International Physics Center, Apdo. 1072, E-20080 San Sebastián (Spain).
⁵ Laboratoire de Chimie Physique, CNRS-UMR 8000, Bâtiment 349, Université de Paris-Sud, F-91405 Orsay (France).
⁶ Permanent address: Groupe Matière Condensée et Matériaux, CNRS-UMR 6626, Bâtiment 11A, Université de Rennes I, F-35042 Rennes (France).
⁷ Institut Laue Langevin, BP 156X, F-38042 Grenoble (France).

We present a neutron scattering investigation on methyl group dynamics in glassy toluene confined in mesoporous silicates of different pore sizes. The experimental results have been analysed in terms of a barrier distribution model, such a distribution following from the structural disorder in the glassy state. Confinement results in a strong decreasing of the average rotational barrier in comparison to the bulk state. We have roughly separated the distribution for the confined state in a bulk-like and a surface-like contribution, corresponding to rotors at a distance from the pore wall respectively larger and smaller than the spatial range of the interactions which contribute to the rotational potential for the methyl groups. We have estimated a distance of 7 Å as a lower limit of the interaction range, beyond the typical nearest-neighbour distance between centers-of-mass (4.7 Å).

I. INTRODUCTION

Porous materials have attracted great interest in the last years, since they provide a framework for the study of the physical properties of solids under restricted geometry¹. The dynamics of systems confined in these materials is expected to differ considerably from that in the bulk state, first of all because the length of the intermolecular interactions and correlations is limited by the finite size of the pore if the latter is sufficiently small. Moreover, the interactions between the pore wall and the confined molecules -which strongly depend on the porous system- would affect the dynamics of these molecules in a non-well defined surface layer on the confined system. Due to their simple dynamics², small molecular rotors as ammonia, methane, ammine ions or methyl groups can be considered as adequate dynamical probes of the effects of confinement by comparing the rotational barriers in the bulk and in confined geometry³.

A thorough neutron scattering study on methyl group dynamics in bulk glassy toluene has been recently presented by some of us⁴. The experimental results were successfully analysed in terms of a well-established barrier distribution model, such a distribution resulting from the structural disorder present in the glass. The average barrier of the distribution was found to be notably higher than that of the β-crystalline reference phase, which shows a short-range structure similar to that of the glassy phase⁴,⁵. This fact could indicate that the relevant intermolecular interactions contributing to the rotational potential of the methyl groups extend beyond nearest-neighbours.

In order to make a comparison with the bulk state and to shed new light about this question and about the interaction lengths controlling the parameters of the distribution, we have carried out neutron scattering measurements on glassy toluene confined in mesoporous silicates with different pore sizes.

II. THEORETICAL ASPECTS

The usual single-particle model for methyl group dynamics in crystalline systems at very low temperatures (T ≈ 2 K) is that of a rigid rotor tunnelling through a one-dimensional rotational potential V(Φ), which is restricted to keep the rotational symmetry of the methyl group². In most of cases only the leading threefold term of the Fourier expansion is retained, higher order corrections being small: V(Φ) = V₃(1 − cos 3Φ)/2. The torsional levels are tunnel-split by the overlapping of the neighbouring single-well wavefunctions, and the energy splitting of the ground torsional level, or rotational frequency ω₁, can be observed in neutron scattering spectra -for barrier heights V₃ below ≈ 700 K in the μeV-range as two resolution-width inelastic peaks centered at ±ω₁. The corresponding incoherent scattering function for rotational tunnelling, normalized to scattering from one hydrogen is²:

\[ S_{MG}^{inc}(Q, \omega) = A(Q) + B(Q)\delta(\omega) + B(Q)[\delta(\omega + \omega₁) + \delta(\omega - \omega₁)] \] (1)
with $\hbar Q$, $\hbar \omega$ respectively the momentum and energy transfer of the neutron, $A(Q) = [1 + 2j_0(Qr)]/3$, $B(Q) = 2[1 - j_0(Qr)]/9$, $j_0(Qr) = \sin(Qr)/(Qr)$ and $r$ the H-H distance in the methyl group.

At temperatures typically above ~ 50 K, a picture of thermally activated classical hopping over the barrier is valid. The corresponding hopping rate follows an Arrhenius-like temperature dependence $\Gamma = \Gamma_\infty \exp(-E_A/kT)$, with $E_A$ the classical activation energy, defined as the difference between the top of the barrier and the ground torsional state. $\Gamma_\infty$ is a temperature-independent preexponential factor. The incoherent scattering function for the classical hopping regime is\(^2\):

$$S_{\text{inc}}^\omega(Q, \omega) = A(Q)\delta(\omega) + 3B(Q)L(\omega; \Gamma)$$

with $L(\omega; \Gamma)$ a normalized Lorentzian of half-width at half-maximum (HWHM) equal to $\Gamma$.

A series of investigations in structural glasses has evidenced the need of introducing a barrier distribution $g(V_3)$ to give account for the different features observed in the spectra of these systems (rotation-rate-distribution-model, RRDM)\(^6\). Such a distribution has its origin in the different local environments for the methyl groups resulting from the structural disorder in the glassy state. According to this approximation, the spectra for the glassy system are obtained as a superposition of crystal-like spectra (tunnel-like as (1) at $T \approx 2$ K, or classical-like as (2) at high temperature) weighted by $g(V_3)$:

$$S_{\text{inc}}^{\omega}(Q, \omega) = \int S_{\text{inc}}^{\omega}(Q, \omega, V_3) dV_3$$

Numerical relationships\(^6\) between $V_3$, $\hbar \omega_1$ and $E_A$ allow the transformation between the corresponding distributions of these quantities $g(V_3)$, $\hbar(\hbar \omega_1)$ and $f(E_A)$. By assuming that the preexponential factor $\Gamma_\infty$ is $V_3$-independent\(^4,6\), $f(E_A)$ can also be transformed, through the Arrhenius law for the temperature dependence of the hopping rate, into the corresponding distribution of hopping rates $H(\log \Gamma)$. Thus, the general equation (3) for the RRDM is reduced to the tunnelling and hopping cases by doing the substitutions $\delta(\omega \pm \omega_1) \rightarrow \int h(\pm \hbar \omega_1) d(\hbar \omega_1)$ in equation (1) and $L(\omega, \Gamma) \rightarrow \int H(\log \Gamma)L(\omega, \Gamma) d(\log \Gamma)$ in equation (2). The consistency of the model is reached when the distributions of tunnelling frequencies and classical hopping rates, obtained respectively at low and high temperature, follow from the same barrier distribution $g(V_3)$.

### III. EXPERIMENTAL DETAILS

Neutron scattering measurements were carried out at the backscattering spectrometer IN16 of the Institute Laue Langevin (ILL, Grenoble, France). A wavelength of 6.27 Å was selected providing an energy resolution of 0.5 μeV (HWHM). The energy window available by Doppler shift covered from -15 to 15 μeV. The scattering angle covered a range from 11 to 149°, resulting in a $Q$-window from 0.2 to 1.9 Å\(^-1\). The instrumental resolution was calibrated by a vanadium sample, which shows purely elastic scattering. Raw data were corrected for detector efficiency, scattering from the sample holder and absorption by means of ILL standard programs.

Spectra were taken on three samples of ring-deuterated toluene confined in mesoporous silicates of the series MCM-41 and SBA-15, which geometry consists of a honeycomb-type lattice of parallel cylindrical pores. They were synthesized with pore diameters $D = 24, 35$ and 47 Å, according to a hydrothermal procedure described in Ref. [7]. The porous geometry parameters were confirmed by neutron diffraction and nitrogen absorption experiments. Deuteration of the silanol groups was achieved by chemical H/D exchange with no further chemical treatment of the surface. Complete filling of the outgased matrices was achieved with an appropriate mass of toluene\(^8\).

Flat samples of thickness 2 mm were used to get transmissions above 90 %, allowing to neglect multiple scattering effects in the $Q$-range investigated, 1.3 - 1.9 Å\(^-1\), where the ratio $B(Q)/A(Q)$ is most favourable in the $Q$-window of IN16. The cooling rate from room temperature to 2 K achieved in the cryostat was sufficient to get the glassy state of confined toluene. Spectra were also taken for the empty matrices, showing purely elastic scattering in the investigated temperature interval.

### IV. RESULTS

Figs. 1, 2 show the incoherent scattering functions, normalized to maximum unity, for confined and bulk glassy toluene -the latter taken from the previous investigation of Ref. [4]-, obtained after subtraction of all the elastic contributions due to coherent scattering and to incoherent scattering from other atoms different from the methyl group protons. In this way the comparison between the dynamics in the confined and in the bulk state is not affected by the different ratios from the methyl group incoherent cross section to the total one. From a direct visual inspection, it is evidenced that confinement results in a strong change in the tunnelling dynamics at 2 K (Fig. 1), and also at the hopping dynamics at high temperature (Fig. 2). As previously reported for the bulk state\(^4\), the experimental data for the confined samples at 2 K could be reproduced in terms of a superposition of tunnelling frequencies, as exposed in Section 2, such a distribution following from an asymmetric Gamma-distribution of rotational barriers $g(V_3)$:

$$g(V_3) = \frac{(p/e)^p}{V_{3\sigma} \Gamma(p)} \left( \frac{V_3}{V_{3\sigma}} \right)^{p-1} \exp \left[ -p \frac{V_3 - V_{3\sigma}}{V_{3\sigma}} \right]$$

with $\Gamma(p)$ the Euler Gamma function, $V_{3\sigma}$ the average barrier and $p$ an adimensional shape parameter measur-
ing the asymmetry of the function. The corresponding standard deviation $\sigma_V$ is obtained as $\sigma_V = V_0^2/\sqrt{P}$. The thick lines in Fig.1 are the RRDM theoretical functions for rotational tunnelling after convolution with the instrumental resolution. The obtained parameters for the three pore diameters investigated are given in Table 1. The error bars are $\sim 5\%$. The resulting distributions are of similar width, but much more asymmetric and with a notably lower average barrier than that of the bulk. A systematic increase of the average barrier is obtained with growing pore size, though far from the bulk limit in all cases, suggesting an important contribution of surface effects to the barrier distribution.

In order to check the consistency of the RRDM for the obtained parameters of $g(V_3)$, we derived the distribution of classical hopping rates through Arrhenius relationship from the distribution of classical activation energies derived from $g(V_3)$. The corresponding RRDM theoretical function for classical hopping was constructed for different values of $\Gamma_\infty$, convoluted with the instrumental resolution and compared with the experimental data. Thick lines in Fig. 2 correspond to the values $\Gamma_\infty = 9$ and 8 meV for confined and for bulk glassy toluene respectively. The error bar for $\Gamma_\infty$ can be estimated in the order of $\pm 3$ and $\pm 2$ meV for the confined and the bulk cases respectively.

V. DISCUSSION

The single-particle potential for methyl group rotation in a given system is built up by intra- and intermolecular interactions extending until a certain radius $r_c$. The results above described show that the distribution of potential barriers for methyl group rotation in glassy toluene is strongly modified by confinement. This has to be certainly related with the presence of the pore-wall and the interactions between the wall and the methyl groups. In a rough approximation we can expect that the methyl groups which are at a distance from the pore wall $r < r_c$ will feel the wall and their single-particle potential will become modified. On the other hand, methyl groups at $r > r_c$ from the pore wall will in principle behave as bulk-like methyl groups. In this framework, $g(V_3)$ can be separated into a “bulk-like” and a “surface-like” contribution, corresponding, respectively, to molecules at a distance of the pore surface beyond and below $r_c$. Previous results corresponding to dynamics of small rotors in confined crystalline systems seem to support this kind of separation. From the cylindrical geometry of the pores, and assuming an homogeneous density of methyl groups within the pores, it is straightforward to calculate the fraction of surface-like molecules as $f_S = 1 - (1 - 2r_c/D)^2$. The corresponding surface-like contribution to the total barrier distribution can be calculated as $g_S(V_3) = [g(V_3) - (1 - f_S)g_B(V_3)]/f_S$, with $g(V_3)$ and $g_B(V_3)$ the distributions for confined and bulk toluene defined by the parameters given in Table 1. For $r_c$ below a certain value, this procedure yields to unphysical negative values of $g_S(V_3)$, so that value can be understood as a lower limit of $r_c$. Unphysical distributions were obtained for $r_c < 5$, 6 and 7 Å for $D = 24$, 35 and 47 Å respectively. Thereby these values correspond to the maximum possible bulk-like contribution to $g(V_3)$ in each case. Fig. 3 shows the distributions for one of the pore diameters and for the bulk case, and also the surface contributions for different values of $r_c$, including some of those with unphysical negative values due to an underestimated value of $r_c$ (see inset). As the interaction radius $r_c$ should not depend on the pore size and $r_c = 7$ Å is also compatible with the $g(V_3)$ obtained for the pore diameters $D = 24$ and 35 Å (see Table II), we can take 7 Å as a first estimation for $r_c$ in glassy toluene. It is noteworthy that this value has to be considered only as a lower limit, because larger values could also be compatible with the different $g(V_3)$ obtained. Measurements at larger pore sizes would be required to give a more accurate estimation of $r_c$. In any case our results seem to support the idea that the relevant interactions on the methyl group extend beyond the typical nearest-neighbour distance between centers-of-mass (4.7 Å), as was suggested by the comparison of the results in the bulk glassy and β-crystalline phases.

| $D$(Å) | $V_0$(K) | $\sigma_V$(K) | $p$ |
|------|--------|------------|-----|
| 24   | 260    | 185        | 2.0 |
| 35   | 270    | 190        | 2.0 |
| 47   | 300    | 210        | 2.0 |
| bulk | 420    | 200        | 4.4 |

TABLE I. Parameters of the barrier distribution for the different pore diameters and for the bulk case.

| $D$(Å) | $V_0^3$(K) | $\sigma_V^3$(K) | $p$ | $f_S$ |
|------|--------|------------|-----|-----|
| 24   | 224    | 155        | 2.1 | 0.83 |
| 35   | 187    | 124        | 2.3 | 0.64 |
| 47   | 183    | 119        | 2.4 | 0.51 |

TABLE II. Parameters of the surface-like contribution $g_S(V_3)$ calculated by assuming $r_c = 7$ Å. The fraction of surface-like methyl groups for this value $r_c$ is also included.
FIG. 1. Incoherent scattering function for methyl group dynamics at 2 K for confined and glassy bulk toluene. Circles are the experimental data. Thick lines are the theoretical functions given by the tunnelling version of the RRDM convoluted with the instrumental resolution (see text). Thin lines are the instrumental resolution. Amplification scale: 3% of the maximum.

FIG. 2. As Fig. 1 for high temperature. In this case, thick lines are the theoretical functions given by the classical version of the RRDM.

FIG. 3. Barrier distribution $g(V_3)$ for confined glassy toluene with $D = 47 \text{ Å}$ and its separation into a bulk-like and a surface-like contribution for $r_c = 7 \text{ Å}$ (see text). The average barrier is indicated in all cases. The inset shows the surface-like distribution $g_S(V_3)$ for different values of $r_c$. The horizontal dashed line marks the zero value for $g_S(V_3)$. 

FIG. 3. Barrier distribution $g(V_3)$ for confined glassy toluene with $D = 47 \text{ Å}$ and its separation into a bulk-like and a surface-like contribution for $r_c = 7 \text{ Å}$ (see text). The average barrier is indicated in all cases. The inset shows the surface-like distribution $g_S(V_3)$ for different values of $r_c$. The horizontal dashed line marks the zero value for $g_S(V_3)$. 

FIG. 3. Barrier distribution $g(V_3)$ for confined glassy toluene with $D = 47 \text{ Å}$ and its separation into a bulk-like and a surface-like contribution for $r_c = 7 \text{ Å}$ (see text). The average barrier is indicated in all cases. The inset shows the surface-like distribution $g_S(V_3)$ for different values of $r_c$. The horizontal dashed line marks the zero value for $g_S(V_3)$. 

FIG. 3. Barrier distribution $g(V_3)$ for confined glassy toluene with $D = 47 \text{ Å}$ and its separation into a bulk-like and a surface-like contribution for $r_c = 7 \text{ Å}$ (see text). The average barrier is indicated in all cases. The inset shows the surface-like distribution $g_S(V_3)$ for different values of $r_c$. The horizontal dashed line marks the zero value for $g_S(V_3)$. 

FIG. 3. Barrier distribution $g(V_3)$ for confined glassy toluene with $D = 47 \text{ Å}$ and its separation into a bulk-like and a surface-like contribution for $r_c = 7 \text{ Å}$ (see text). The average barrier is indicated in all cases. The inset shows the surface-like distribution $g_S(V_3)$ for different values of $r_c$. The horizontal dashed line marks the zero value for $g_S(V_3)$. 

FIG. 3. Barrier distribution $g(V_3)$ for confined glassy toluene with $D = 47 \text{ Å}$ and its separation into a bulk-like and a surface-like contribution for $r_c = 7 \text{ Å}$ (see text). The average barrier is indicated in all cases. The inset shows the surface-like distribution $g_S(V_3)$ for different values of $r_c$. The horizontal dashed line marks the zero value for $g_S(V_3)$.
1. Proceedings of the International Workshop on Dynamics in Confinement, Grenoble (France) January 26-29, 2000. J. Phys. IV France **10**, (2000).

2. M. Prager, A. Heidemann, Chem. Rev **97**, (1997) 2933.

3. C. Gutt, B. Asmussen, I. Krasnov, W. Press, W. Langel, R. Kahn, Phys. Rev. B **59**, (1999) 8607; I.A. Krasnov, B. Asmussen, C. Gutt, W. Press, W. Langel, M. Ferrand, J. Phys.: Condens. Matter **12**, (2000) 1613; R.M. Dimeo, D.A. Neumann, Phys. Rev. B **63**, (2001) 14301; R.M. Dimeo, D.A. Neumann, Y. Glanville, D.B. Minor, Phys. Rev. B **66**, (2002) 104201.

4. A.J. Moreno, A. Alegría, J. Colmenero, M. Prager, H. Grimm, B. Frick, J. Chem. Phys. **115**, (2001) 8958.

5. J. Bruneaux-Poulle, A. Defrain, M. Dupont, J. Chim. Phys. Chim. Phys. Biol. **78**, (1981) 217.

6. J. Colmenero, R. Mukhopadhyay, A. Alegría, B. Frick. Phys. Rev. Lett. **80**, (1998) 2350; A.J. Moreno, A. Alegría, J. Colmenero, Phys. Rev. B **63**, (2001) R60201; A.J. Moreno, A. Alegría, J. Colmenero, B. Frick, Macromolecules **34**, (2001) 4886.

7. C.T. Kresge, M.E. Leonowitz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature **359**, (1992) 710; M. Grün, I. Lauer, K. Unger, Adv. Mater. **9**, (1997) 254; D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G. D. Stucky, Science **279**, (1998) 548.

8. D. Morineau, Y. Xia, C. Alba-Simionesco, J. Chem Phys. **117**, (2002) 8966; and this issue.