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Juan Colmenero, Fernando Alvarez, Yasmin Khairy, and Arantxa Arbe

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Modeling the collective relaxation time of glass-forming polymers at intermediate length scales: Application to polyisobutylene

Juan Colmenero,^{1,2,3,a)} Fernando Alvarez,^{2,3} Yasmin Khairy,³ and Arantxa Arbe³

¹Donostia International Physics Center, Paseo Manuel de Lardizabal 4, E-20018 San Sebastián, Spain

²Departamento de Física de Materiales (UPV/EHU), Apartado 1072, E-20080 San Sebastián, Spain

³Centro de Física de Materiales (CSIC, UPV/EHU) and Materials Physics Center MPC, Paseo Manuel de Lardizabal 5, E-20018 San Sebastián, Spain

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In a recent paper [V. N. Novikov, K. S. Schweizer, and A. P. Sokolov, *J. Chem. Phys.* **138**, 164508 (2013)] a simple analytical ansatz has been proposed to describe the momentum transfer (Q) dependence of the collective relaxation time of glass-forming systems in a wide Q -range covering the region of the first maximum of the static structure factor $S(Q)$ and the so-called intermediate length scale regime. In this work we have generalized this model in order to deal with glass-forming systems where the atomic diffusive processes are sub-linear in nature. This is for instance the case of glass-forming polymers. The generalized expression considers a sub-linear jump-diffusion model and reduces to the expression previously proposed for normal diffusion. The generalized ansatz has been applied to the experimental results of the Q - and temperature-dependence of polyisobutylene (PIB), which were previously published. To reduce the number of free parameters of the model to only one, we have taken advantage of atomistic molecular dynamics simulations of PIB properly validated by neutron scattering results. The model perfectly describes the experimental results capturing both, Q - and temperature-dependences. Moreover, the model also reproduces the experimental Q -dependence of the effective activation energy of the collective relaxation time in the temperature range of observation. This non-trivial result gives additional support to the way the crossover between two different relaxation mechanisms of density fluctuations is formulated in the model. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816127>]

I. INTRODUCTION

The investigation of collective dynamics of glass-forming systems in general at the so-called intermediate scales (or mesoscales) is still a wide open area on the relaxation maps of such systems. Intermediate scales means the region of lengths larger than intermolecular distances but smaller than the hydrodynamic range. In a scattering experiment this translates into a momentum transfer (Q) range extending down from the Q_{max} corresponding to the maximum of the static structure factor $S(Q)$ towards Q -values of the order of $0.1 \text{ \AA}^{-1}$. From an experimental point of view, this is a rather difficult regime due to different technical questions. First of all, the intensity scattered in this Q -range is, in general, very low. In addition, there are multiple scattering problems originating from the primary scattering at the first structure factor peak. Moreover, the slow time scales of the atomic motions demand for high resolution techniques. At the present moment, high resolution neutron spin echo (NSE) is the only technique that can be used to overcome these experimental problems and to deal with this difficult experimental task. Likely due to these problems, experimental coherent neutron scattering dynamic data of glass-formers in the intermediate Q -region are scarce. In the particular case of glass-forming polymers, the collective dynamics of polyisobutylene (PIB) has been thoroughly investigated by NSE at different tem-

peratures and in a wide Q -range, covering the regime of the first maximum of $S(Q)$ and that of the intermediate scales.¹ The results reported in Ref. 1 for the collective relaxation time $\tau_c(Q)$ at the different temperatures investigated are reproduced here in Fig. 1. For all three temperatures the same qualitative behavior of $\tau_c(Q)$ is observed. $\tau_c(Q)$ shows a peak at about $Q = 1 \text{ \AA}^{-1}$, i.e., in the Q -range of the first maximum of $S(Q)$. In principle, this could be expected from a de Gennes-like narrowing.² However, below this high- Q peak, in the intermediate Q -regime, $\tau_c(Q)$ develops some kind of plateau, even suggesting the possibility of another maximum at lower Q -values ($Q \approx 0.3 \text{ \AA}^{-1}$). As it was discussed in Ref. 1, taking into account the $S(Q)$ -values this behavior cannot be expected from any de Gennes-like narrowing picture.

Another puzzling result reported in Ref. 1 was the Q -dependence found for the activation energy, E_a , of the collective relaxation time $\tau_c(Q, T)$ (E_a was defined in the explored temperature range). The reported values of $E_a(Q)$ are reproduced here in Fig. 2. As it was discussed in Ref. 1, the behavior of $E_a(Q)$ suggests the influence of more than one relaxation mechanism.

On the other hand, concerning computer simulations, we have to say that the intermediate length/ Q regime is even a more difficult range than for neutron scattering. The reason is very simple. In order to calculate coherent scattering at low Q -values of the order of $0.1\text{--}0.2 \text{ \AA}^{-1}$ for a cubic simulated cell, the size of this cell has to be rather large (more than $100 \text{ \AA}$

^{a)}Electronic mail: juan.colmenero@ehu.es

FIG. 1. Momentum transfer dependence of the average characteristic times for collective motions obtained from NSE measurements on deuterated PIB¹ at 335 (circles), 365 (squares), and 390 K (diamonds). Dotted lines correspond to the average characteristic times for self motions calculated from the simulations at the same temperatures (top to bottom). Solid lines represent the proposed description by Eq. (4).

side), containing thereby a huge number of atoms. Moreover, for the low- Q values, there are only very few reciprocal vectors complying with the periodic boundary conditions. Usually this leads to unsatisfactory statistics in the case of the calculated collective scattering function. In spite of these difficulties, the collective dynamics in a wide Q -range covering the intermediate regime has been reported for molecular dynamics (MD) simulations of a simple “bead-spring” model of glass-forming polymers.³ Interestingly, the results obtained for $\tau_c(Q)$ resemble in some way those experimentally found for PIB. Moreover, they clearly show a broad maximum at Q -values lower than that of $S(Q)$.

Finally, from a theoretical point of view the dynamics of glass-forming systems in general in the intermediate length scales region is also far from being understood. Although

FIG. 2. Momentum transfer dependence of the activation energy E_a of the collective characteristic times of PIB in the temperature interval $335 \leq T \leq 390$ K. Points correspond to the experimental results reported in Ref. 1 and the continuous line to the model results. The shadowed area represents the uncertainty level (see the text). Horizontal dotted lines mark for comparison of the activation energies deduced from rheological measurements E_{rheo} ²⁴ and for the average values of the characteristic time for self-motions at $Q = 1 \text{ Å}^{-1}$ of hydrogens (E_H , from experiments¹) and of all atoms (E_{self} , from simulations).

there are more or less accepted theoretical approaches for the local and intermolecular level – as for instance the mode coupling theory⁴ – and for the continuous limit,⁵ it does not exist any theory or even a statistical-based model bridging the gap of the intermediate scales. Progress in this direction is essential not only in order to reach a final understanding of glass-forming dynamics, but also for analyzing (and motivating) neutron scattering results in the intermediate length scale regime.

In a recent paper⁶ they have formulated a simple analytical model for the temperature and Q -dependent collective density fluctuation relaxation time $\tau_c(Q, T)$ in a wide Q -range, covering both the $S(Q)$ and the intermediate Q -region of glass-forming systems. They have successfully applied this model to available neutron scattering data corresponding to the ionic system Ca-K-NO₃ (CKN). In this work, we show that in order to apply this approach to glass-forming polymers, it needs to be modified to take into account the particularities of the local and diffusive motions in polymer melts. In this way we develop a generalization of the model proposed in Ref. 6. We show that this generalized model consistently describes the $\tau_c(Q, T)$ available data of PIB mentioned above.

II. THEORETICAL MODEL

The ansatz proposed in Ref. 6 is based on an interpolation formula that embeds both, the mesoscopic and the high- Q limits discussed by those authors, in a convenient analytical expression:

$$\frac{1}{\tau_c(Q)} = \frac{1}{\tau_\alpha(0)} \frac{K_B}{M_L} e^{-Q^2 \xi_c^2} + \frac{1}{S(Q)} \frac{Q^2 D_s}{1 + Q^2 \xi_D^2}. \quad (1)$$

The first term of this expression contains the inverse of a non-diffusive (Q -independent) relaxation time $\tau(Q \rightarrow 0) = \frac{M_L}{K_B} \tau_\alpha(0)$. Here K_B is the bulk modulus and $M_L \approx K_B + (4/3)G$ the longitudinal elastic modulus, where G is the elastic shear modulus. The time $\tau_\alpha(0)$ has the meaning of an α (structural) relaxation time associated with a typical $Q \sim 0$ correlation function. The authors of Ref. 6 identify it with the time corresponding, for instance, to a dielectric or viscoelastic response. This time should reflect the viscoelastic coupling of stress and density fluctuations on scales long enough compared to atomic dimensions, but not yet in the hydrodynamic limit. The first term of Eq. (1) also includes a Gaussian cutoff factor $e^{-Q^2 \xi_c^2}$ to ensure that the lower- Q non diffusive contribution is present only on length scales beyond a characteristic length ξ_c , which is assumed to be $\xi_c \sim 2\pi/Q_{max}$.

The second term of Eq. (1) corresponds to a high- Q diffusive contribution “modulated” by the static structure factor $S(Q)$. The corresponding collective relaxation time $\tau_c^D(Q)$ is in fact taken as $\tau_c^D(Q) = S(Q)\tau_s^D(Q)$ where $\tau_s^D(Q) = (1 + Q^2 \xi_D^2)/(Q^2 D_s)$, being D_s a diffusion coefficient. It is straightforward to see that $\tau_s^D(Q)$ expressed in this way corresponds to the self (incoherent) relaxation time of a jump-diffusion model^{7,8} with a preferred jump distance ξ_D and a distribution of jump distances given by the function $f_o(\xi) = \frac{\xi}{\xi_D} \exp(-\frac{\xi}{\xi_D})$. For liquids and disordered systems the directions of the jumps are assumed to be randomly oriented. In

the Q -range where $Q\xi_D \ll 1$, $\tau_s^D(Q) \approx Q^{-2}D_s^{-1}$. It is noteworthy to remark that in this Q -range the approximation made by the authors of Ref. 6 to calculate the collective relaxation time from $\tau_s^D(Q)$ [$\tau_c^D(Q) = S(Q)\tau_s^D(Q)$] in fact corresponds to the approximation proposed by Skögl⁹ via renormalization of Q by the $\sqrt{S(Q)}$. However, we note in passing that this is not the case in the high- Q regime ($Q\xi_D \gtrsim 1$).

Although the above discussed ansatz has been proposed for glass-forming liquids in general, we would like to point out that in order to deal with glass-forming polymers, it needs to be modified, in particular, regarding the diffusive contribution. It is nowadays well established from neutron scattering and simulation results that self-atomic motions in the α -relaxation regime of glass-forming polymers follow sub-linear diffusion processes with the mean squared atomic displacement given by $\langle r^2(t) \rangle \propto t^\beta$ ($\beta < 1$).¹⁰ Moreover, in the Q -regime $Q \lesssim 1 \text{ \AA}^{-1}$ the Gaussian approximation seems to work in general and thereby the incoherent scattering function can be written as

$$F_s(Q, t) \propto \exp \left[- \left(\frac{t}{\tau_s^D(Q)} \right)^\beta \right], \quad (2)$$

where $\tau_s^D(Q) \propto Q^{-2/\beta}$.¹¹ In this case, a Skögl-like renormalization would give a collective relaxation expressed as $\tau_c^D(Q) = [S(Q)]^{1/\beta} \tau_s^D(Q)$. In the high- Q range, some deviations of $\tau_s^D(Q) \propto Q^{-2/\beta}$ have been observed and they have been usually described in terms of a sub-linear jump-diffusion model,^{12–14} which as in the case of the simple jump-diffusion model used by Novikov *et al.*,⁶ also considers a distribution of jump distances $f_o(\xi) = \frac{\xi}{\xi_D^2} \exp(-\frac{\xi}{\xi_D})$. The jumps leading to sublinear diffusion would correspond to the dynamics allowing the decaging mechanism. It is noteworthy that the preferred jump distance ξ_D found in polymers seems to coincide with the so-called localization length in the framework of the mode-coupling theory.^{13,15} In this framework, the incoherent relaxation time $\tau_s^D(Q)$ can be expressed as

$$\tau_s^D(Q) = \tau_o \left[1 + \frac{1}{Q^2 \xi_D^2} \right]^{\frac{1}{\beta}}, \quad (3)$$

where $\tau_o = \xi_D^2/D_s$. In the Q -range where $Q\xi_D \ll 1$, we recover the Q -dependence of $\tau_s^D(Q)$ given by $Q^{-2/\beta}$. Following the spirit of the ansatz proposed in Ref. 6, here we will extend the expression $\tau_c^D(Q) = [S(Q)]^{1/\beta} \tau_s^D(Q)$ also to the high- Q range.

In this framework, the generalization of Eq. (1) for polymers proposed by us reads:

$$\frac{1}{\tau_c(Q)} = \frac{1}{\tau_o(0)} \frac{K_B}{M_L} e^{-Q^2 \xi_c^2} + \frac{1}{[S(Q)]^{1/\beta}} \frac{D_s}{\xi_D^2} \left[1 + \frac{1}{Q^2 \xi_D^2} \right]^{-\frac{1}{\beta}}, \quad (4)$$

where we have not modified the first non-diffusive contribution of Eq. (1). It is straightforward to see that Eq. (4) reduces to Eq. (1) for $\beta = 1$.

III. APPLICATION OF THE ANSATZ TO PIB DATA

In the following we will check the validity of Eq. (4) by using the neutron scattering (neutron spin echo, NSE) re-

sults of $\tau_c(Q)$ for PIB, which were reported in Ref. 1. As far as to our knowledge, these are the best available data in the literature, covering both, the Q -range of the maximum of $S(Q)$ and the intermediate Q -range. They were obtained from the description of the normalized dynamic structure factor in terms of stretched exponential functions (analogous to Eq. (2)) with a fixed value of 0.55 for the stretching parameter β . In the following, in order to consistently compare characteristic times corresponding to different spectral shapes (different β -parameters) we will always consider the average times. The average time of a given correlation function $\Phi(t)$ is defined as $\langle \tau \rangle = \int_0^\infty \Phi(t) dt$ and in the case of a stretched exponential functional form $\Phi(t) = \exp[-(t/\tau_w)^\beta]$ is given by $\langle \tau \rangle = \frac{\Gamma(1/\beta)}{\beta} \tau_w$. The average values of $\tau_c(Q)$ of PIB for the available temperatures 335, 365, and 390 K are shown in Fig. 1. In order to apply Eq. (4) to these data we have used the following strategy trying to reduce as much as possible the number of free parameters. Concerning the first non-diffusive contribution of Eq. (4) we have taken similar approximations as those used in Ref. 6. First, from Ref. 16 we have calculated $M_L/K_B \approx 1.6$ for PIB and second, we impose $\xi_c \sim 2\pi/Q_{max}$, where Q_{max} corresponds to the first maximum of the experimental $S(Q)$ reported in Ref. 1 ($Q_{max} = 1 \text{ \AA}^{-1}$). On the other hand, concerning the diffusive contribution to Eq. (4), the values of $S(Q)$ are known from the NSE measurement.¹ The rest of the parameters of this contribution (D_s , ξ_D , and β) in fact correspond to the self incoherent relaxation time $\tau_s^D(Q)$ behavior. Therefore, in principle they could be fixed by fitting the experimental $\tau_s^D(Q)$. The problem is that the incoherent scattering cross section of carbon is 0, and therefore the $\tau_s^D(Q)$ experimentally determined by neutron scattering on a protonated sample only corresponds to hydrogen motions. However, the experimental collective time $\tau_c(Q)$ shown in Fig. 1 actually corresponds to an average over all atoms in the sample (hydrogen and carbon). This is due to the fact that the collective measurements by NSE are carried out on fully deuterated samples where the dominating scattering is the coherent one, and the scattering lengths of carbon and deuteron are almost the same ($b_C = 6.6511 \text{ fm}$; $b_D = 6.671 \text{ fm}$). Therefore, the $\tau_s^D(Q)$ that we have to consider in Eq. (4) is that corresponding to the average of $\tau_s^D(Q)$ of hydrogen and carbon atoms. Unfortunately, this cannot be obtained experimentally.

In order to overcome this experimental limitation, in this work we have taken advantage of fully atomistic molecular dynamic (MD) simulations of PIB, recently performed by us, which have been properly validated by neutron scattering results previously published.¹ The atomistic simulations were carried out by means of the COMPASS forcefield. The cubic simulation cell contained 20 PIB chains of 70 monomers each (total number of atoms $N = 16\,840$). Initially, by means of NPT dynamic runs (i.e., keeping constant N , pressure, and temperature) values of the density close to the experimental ones at the different temperatures simulated were obtained. The side of the cubic cell in such conditions was of the order of 54 Å. After that, successive NVT equilibration runs (i.e., keeping constant N , volume, and temperature) were carried out followed by the production of dynamic runs. The simulation time was extended until 100 ns. More simulation details

FIG. 3. Validation of the simulation: Structure factor calculated at 320 K compared with experimental results on a deuterated sample in a wide Q -range by a triple axis spectrometer.^{1,20} The experimental data have been corrected from incoherent contributions taking into account NSE results with polarization analysis.¹ The inset comparing data simulated and measured by NSE at 390 K demonstrate that the simulation also captures the temperature dependence of $S(Q)$. The NSE results show a weaker peak due to the instrumental resolution ($\Delta\lambda/\lambda = 20\%$).

as well as a complete quantitative analysis of the simulation results will be presented elsewhere.¹⁵ Here we only show two examples of the validation results, which demonstrate the reliability of the simulation cell in particular with respect to the atomic structure and the atomic self-motions. We note in passing that the calculation of the incoherent scattering functions in the intermediate Q -range from the simulations is not affected by the technical problems commented in the introduction for the collective magnitudes. Figure 3 shows the good agreement found between the measured static structure factor $S(Q)$ and the simulation results. Moreover, Fig. 4 displays the comparison between the NSE results on a protonated PIB sample¹ revealing the incoherent scattering function of the hydrogen and the same function calculated from the simulations. This comparison is shown in the same temperature range where $\tau_c(Q)$ is reported (see Fig. 1) and for two dif-

FIG. 4. Validation of the simulation: NSE results measured (symbols)¹ and calculated from the simulations (lines) on a protonated sample. Circles: $Q = 0.73 \text{ \AA}^{-1}$; squares: $Q = 1.58 \text{ \AA}^{-1}$. Empty symbols correspond to 335 K and full symbols to 390 K.

FIG. 5. Momentum transfer dependence of the average characteristic times for self motions obtained from MD simulations at 335 (circles), 365 (squares), and 390 K (filled diamonds). Solid lines correspond to the fits by the anomalous jump diffusion model (Eq. (3)). Empty diamonds correspond to the average values of the characteristic times obtained from the NSE experiments on the protonated sample¹ reflecting hydrogen self-motions.

ferent Q -values. Again, the agreement is perfect in particular taking into account that there is not any time-shift between simulated and measured data.

Now after the validation of the MD-simulations we can easily calculate from the simulated atomic trajectories – corresponding to hydrogen and carbon atoms – the average incoherent scattering function at the temperatures and Q -values of interest. A standard fitting of these functions in the time range $2 \text{ ps} \leq t \leq 40 \text{ ns}$ by stretched exponential functions (Eq. (2)) gives the values of the parameters β [$\beta(335 \text{ K}) = 0.44$; $\beta(365 \text{ K}) = 0.47$; $\beta(390 \text{ K}) = 0.49$] and $\tau_s^D(Q)$. The corresponding average relaxation times are shown in Fig. 5. They have been fitted to the expression discussed above, corresponding to the sub-linear jump-diffusion model (Eq. (3)). The continuous lines in Fig. 5 are the fitting curves. The values obtained for the fitting parameters are $D_s(335 \text{ K}) = 0.61 \text{ \AA}^2/\text{ns}$; $D_s(365 \text{ K}) = 3.22 \text{ \AA}^2/\text{ns}$; $D_s(390 \text{ K}) = 8.81 \text{ \AA}^2/\text{ns}$; and a temperature independent value of $0.6 \text{ \AA}$ for ξ_D , corresponding to an average jump distance $\langle\xi_D\rangle = \sqrt{6}\xi_D$ of $1.5 \text{ \AA}$. The value of ξ_D is in the range usually reported for the jump distances involved in the hydrogen motions in polymers (e.g., $\xi_D = 0.5 \text{ \AA}$ for polybutadiene;¹⁷ $0.6 \text{ \AA}$ for poly(vinyl(ethylene)),^{17,18} $0.65 \text{ \AA}$ for poly(vinyl methyl ether)¹⁹ and $0.42 \text{ \AA}$ for polyisoprene^{12,13} – in this case, for only the main-chain hydrogens). Here, the jump distance would result from the average of those of hydrogen and carbon atoms. For comparison, we have also included in Fig. 5 the average values of the characteristic times corresponding to the experimental results at 390 K¹ reflecting only hydrogen motions. As can be appreciated, the experimental function displays faster times. This can be attributed to slower motions of the carbons contributing to the total-self function, and also to possible coherent contributions to the neutron spin echo results. A reliable jump distance cannot be obtained from these experimental data.

Now we can come back to the application of Eq. (4) to describe the experimental data of $\tau_c(Q)$ shown in Fig. 1. Taking into account the simulation results discussed above and the

experimental values of $S(Q)$ at each temperature, the diffusive contribution of Eq. (4) is completely fixed. Moreover, according to the approximations introduced above for the non-diffusive contribution ($M_L/K_B \approx 1.6$; $\xi_c = 2\pi/Q_{max}$) the only remaining free parameter is $\tau_\alpha(0)$. The continuous lines in Fig. 1 are the model curves obtained by fitting $\tau_\alpha(0)$. The description found on $\tau_c(Q)$ is remarkable taking into account the uncertainties involved and the approximations made in the model. Only in the case of the lowest temperature (335 K) data it seems that there is a systematic deviation of the model curve from the experimental data. The reason could be the higher uncertainties involved in the determination of the experimental characteristic times and the shape of the relaxation function in the low temperature range. The NSE results were described assuming a temperature-independent β -parameter, but a decrease of the value of β could be expected with decreasing temperature. In fact, from the simulations a decrease from 0.55 at 390 K to 0.5 at 335 K is found for the stretching parameter of the collective dynamic structure factor.¹⁵ At 335 K, the NSE window is sensitive to the faster part of the decay of the dynamic structure factor. Using a higher β -value than the actual one would deliver shorter times from the fit to stretched exponentials and, in addition, the factor $\frac{\Gamma(1/\beta)}{\beta}$ used for the conversion to average times would be smaller. This would lead to overall faster collective times deduced from the NSE measurements at this temperature.

The values of $\tau_\alpha(0)$ found are represented in Fig. 6 as function of temperature. When Novikov *et al.* introduced Eq. (1) in Ref. 6, they suggested that $\tau_\alpha(0)$ should agree with the dielectric relaxation time. Therefore, for comparison, we have included in Fig. 6 the values of the average relaxation time obtained from dielectric spectroscopy measurements on PIB reported in Ref. 20. The temperature/frequency range covered by this technique does not overlap with that where $\tau_\alpha(0)$ is determined. Nevertheless, we may estimate what would be the expected dielectric results in the interesting

FIG. 6. Temperature dependence of the average characteristic times deduced for $\tau_\alpha(0)$ from the descriptions in Fig. 1 (diamonds), compared with those obtained from dielectric spectroscopy²⁰ (filled squares) and from NSE measurements¹ for the self-motions of hydrogens at $Q = 1.0 \text{ \AA}^{-1}$ (empty squares). The continuous line is a Vogel-Fulcher fit $\tau(T) = \tau_0 \exp(\frac{B}{T-T_0})$ of dielectric and self-correlation times with $\tau_0 = 1 \times 10^{-14} \text{ s}$, $B = 2569 \text{ K}$, and $T_0 = 131 \text{ K}$.

range in the following way. It has been reported^{21,22} that the dielectric time scale in glass-forming polymers usually coincides with the incoherent times obtained in protonated samples at $Q \sim 1 \text{ \AA}^{-1}$. Although the reason for this agreement is not yet understood, it is an experimental fact. In some polymers it has also been pointed out that this coincidence takes place at the Q -value corresponding to the first structure factor peak Q_{max} .²³ For PIB, both criteria correspond to the same Q -value. Figure 6 also includes the experimental values of the incoherent relaxation times corresponding to the hydrogen motions at the Q -value of $1 \text{ \AA}^{-1}$.¹ Both, dielectric and incoherent scattering results, can be jointly described by a unique Vogel Fulcher law. Thus, the empirical finding seems to also apply in the case of PIB. What is interesting is that the $\tau_\alpha(0)$ found also agrees with these data. Thereby, the results obtained here seem to give support to the interpretation proposed in Ref. 6 for $\tau_\alpha(0)$.

Now, by considering the rate between the values of $\tau_c(Q)$ obtained from the model at two different temperatures we can calculate the Q -dependence of the effective activation energy, $E_a(Q)$, in the explored temperature range. We have followed this procedure by taking into account the results of $\tau_c(Q)$ at the three temperatures that we have explored. The average value of $E_a(Q)$ obtained in this way is shown by the continuous line in Fig. 2. The shadowed area means the level of uncertainty of this procedure. It has been calculated taking into account the different values of $E_a(Q)$ obtained with the different pairs of temperatures. As can be seen in the figure, the experimental behavior is nicely reproduced within the uncertainties. We note that the presence of the maximum of E_a around Q_{max} is mainly due to the changes of the static structure factor with temperature.¹⁵ Reproducing this feature is a non-trivial result that gives support to the way the crossover between two different relaxation mechanisms of density fluctuations is formulated in Eqs. (1) and (4).

Finally, as it has been mentioned in the introduction, a broad pre-peak in the Q -dependence of the collective relaxation time at Q -values lower than that of the maximum of $S(Q)$ (i.e., in the intermediate Q -range discussed here) was reported in Ref. 3 from simulations of a simple bead-spring model of glass-forming polymers. This peak resembles that shown by our model (see Fig. 1). In the case of the bead-spring model results, the Q -range where the pre-peak occurs is of the order of $2\pi/R_g$ (R_g being the radius of gyration of the simulated polymers). Based on this coincidence, it was speculated that this pre-peak could be related in some way with the “packing” of the soft polymer coils in the melt like that of monomers at Q_{max} . However, in the framework of the approximation discussed here, the pre-peak of $\tau_c(Q)$ would only be a consequence of the crossover between two different relaxation mechanisms.

IV. SUMMARY AND CONCLUSIONS

In this work we have generalized the analytical model proposed in Ref. 6 for describing the Q -dependence of the collective relaxation time of glass-forming systems in the intermediate Q -range. The generalized ansatz allows to deal with

glass-forming systems where the atomic diffusive processes are sublinear. This is for instance the case of glass-forming polymers. The generalized expression considers a sub-linear jump-diffusion model and reduces to that proposed in Ref. 6 for normal diffusion.

The generalized ansatz has been applied to the case of polyisobutylene. The collective dynamics of this polymer was previously investigated¹ and precise data of the collective relaxation time in a wide Q -range, including the range of the first structure factor peak and that corresponding to the intermediate scales, were available. By taking advantage of properly validated MD-simulation results of PIB we were able to reduce the number of fitting parameters of the model to only one, $\tau_\alpha(0)$. The model captures not only the Q -dependence of the collective time but also its temperature dependence. Moreover, $\tau_\alpha(0)$ seems to agree with the dielectric relaxation time scale as it was suggested in Ref. 6, supporting the interpretation of $\tau_\alpha(0)$ outlined in that work. Finally, the model nicely reproduces the Q -dependence of the effective activation energy, E_a , in the temperature range of observation. This non-trivial result gives additional support to the proposed model.

In conclusion we can say that the results presented in this work not only give support to the generalized model developed here but also show that the theoretical framework developed in Ref. 6 seems to contain the main ingredients to construct a more elaborated theory of the collective dynamics of glass-forming systems at intermediate length scales.

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