

Molecular Dynamics in Confining Space: From the Single Molecule to the Liquid State

A. Huwe and F. Kremer*

Department of Physics, University of Leipzig, D-04103 Leipzig, Germany

P. Behrens

Department of Chemistry, University of Hannover, D-30167 Hannover, Germany

W. Schwieger

Department of Chemistry, Martin-Luther-University Halle-Wittenberg, D-06108 Halle, Germany

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The transition from the dynamics of isolated molecules to that of a bulk liquid is observed for the first time by analyzing the dielectric relaxation (10^{-2} – 10^9 Hz) of ethylene glycol (EG) guest molecules confined to zeolitic host systems of different topology. Beyond a threshold channel size the liquid character is lost, indicated by a dramatically increased relaxation rate and an Arrhenius-like temperature dependence. Computer simulations of the molecular arrangement in a confining space prove that an ensemble as small as six molecules is sufficient to exhibit the dynamics of a bulk liquid. [S0031-9007(99)08701-3]

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The nature of glassy liquids is still not well understood and is the focus of worldwide scientific discussion [1–6]. Central questions are the length scale on which the molecular fluctuations of a liquid take place, and under what conditions the transition from a single molecule behavior to that of a liquid occurs [7–17]. Guest molecules [e.g., ethylene glycol (EG) HO-CH₂-CH₂-OH] being confined to zeolitic host systems offer a unique possibility of studying this: While in sodalite—because of steric reasons—only one molecule of EG is present per zeolitic cage, other zeolites (e.g., silicalite and zeolite beta) possess inner channel structures in which guest molecules can interact with each other. In measuring the dynamics of the (dielectrically active) guest molecules in (dielectrically inactive) host systems over a frequency range from 10^{-2} to 10^9 Hz, broadband dielectric spectroscopy proves to be an ideal experimental tool for these studies [14–19].

Silica sodalite is a clathrasil compound built from identical, so-called β cages, with a free inner diameter of 0.6 nm. Ethylene glycol is one of the structure-directing agents which controls the formation of silica sodalite [20,21]. The EG molecules become occluded during synthesis and cannot escape from the cages (unless they are thermally decomposed) [21]. Besides silica sodalite, silicalite-I and zeolite beta were used as zeolitic host systems with three-dimensional pore systems. Silicalite consists of pure silica and has two different types of elliptical channels with cross sections of $0.56 \text{ nm} \times 0.53 \text{ nm}$ and $0.55 \text{ nm} \times 0.51 \text{ nm}$ [22]. In zeolite beta, an aluminosilicate with a Si:Al ratio of 40, the channels in [100] and [010] directions have a diameter of $0.76 \text{ nm} \times 0.64 \text{ nm}$, whereas the channels in the [001] direction have smaller pores ($0.55 \text{ nm} \times 0.55 \text{ nm}$) [23]. Silicalite and zeolite beta are filled with guest molecules after synthesis and calcination. These nanoporous hosts are

heated to 330 °C with a temperature increase of 20 °C/h and evacuated at 10^{-5} mbar for 36 h to remove water and other volatile impurities. Afterwards they are filled with EG from the vapor phase in a closed vacuum chamber at 175 °C. The samples are cooled to room temperature and remain in the vacuum chamber for 24 h before the dielectric measurements are carried out.

The dielectric measurements were performed using two different systems based on different measurement principles: Between 10^{-2} and 10^7 Hz, frequency response analysis is carried out (Solatron–Schlumberger frequency response analyzer FRA 1260 with a Novocontrol active sample cell BDC–S). From 10^6 to 1.8×10^9 Hz a Hewlett-Packard impedance analyzer (HP 4291A) is employed. The sample temperatures are controlled by means of a nitrogen gas jet having a stability better than ± 0.05 K. Details of the setup may be found in Ref. [24]. For the analysis of the dielectric measurements the imaginary part ϵ'' of the dielectric function is fitted using a superposition of a conductivity contribution and a generalized relaxation function according to Havriliak and Negami [25],

$$\epsilon'' = \frac{\sigma_0}{\epsilon_0} \frac{a}{\omega^s} - \text{Im} \left[\frac{\Delta \epsilon}{[1 + (i\omega\tau)^\alpha]^\gamma} \right]. \quad (1)$$

In this notation, ϵ_0 is the vacuum permittivity, σ_0 is the dc conductivity, and $\Delta \epsilon$ is the dielectric strength. α and γ describe the symmetric and asymmetric broadening of the relaxation time distribution function. From the fits according to Eq. (1), the mean relaxation rate $1/\tau_{\text{max}}$ can be deduced which is given at the frequency of maximum dielectric loss ϵ'' for a certain temperature. It is shown (Fig. 1) that the relaxation rates for EG in zeolite beta and silicalite are separated by several orders of magnitude and that the relaxation strength of EG in sodalite is

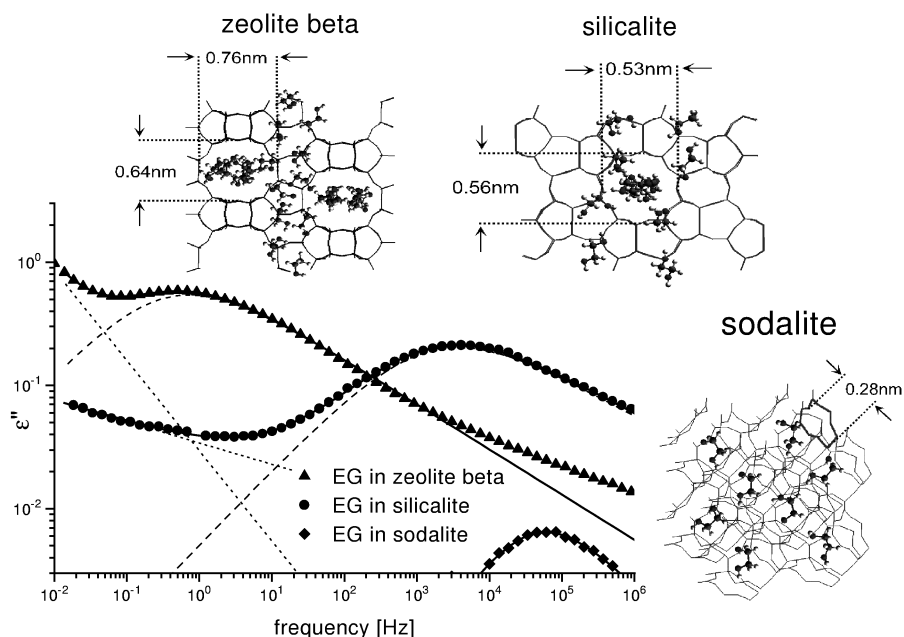


FIG. 1. Dielectric loss ϵ'' of ethylene glycol (EG) at 160 K confined in sodalite (diamonds), in silicalite (circles), and in zeolite beta (triangles). The experimental errors are smaller than the size of the symbols. The solid lines are fits based on a superposition of a conductivity contribution (dotted line) and a generalized relaxation process according to Havriliak and Negami [25]. A deviation in the high frequency wing as for EG in zeolite beta has been observed for bulk liquids as well [19]. The models show the corresponding zeolitic frameworks, their dimensions, and the confined molecules.

comparably weak. The latter is caused by EG molecules which are immobilized due to the interaction with the host matrix.

Figure 2 shows the logarithmic mean relaxation rate as a function of the inverse temperature for EG as bulk liquid and confined in zeolites. Ethylene glycol in zeolite beta (triangles) has a mean relaxation rate like the bulk liquid (squares) following the characteristic temperature dependence according to Vogel-Fulcher-Tammann [26–28] (VFT dependence):

$$\frac{1}{\tau} = A \exp\left(\frac{DT_0}{T - T_0}\right), \quad (2)$$

where A is a prefactor, D is the fragility parameter, and T_0 is the Vogel temperature. In contrast, the isolated molecules in sodalite show a single molecule relaxation with an Arrhenius-type temperature dependence which is, for $T \approx 155$ K, about 6 orders of magnitude faster compared to the bulk liquid. The activation energy of this relaxation is 26 ± 1 kJ/mol and corresponds to the value for bulk EG at high frequencies and high temperatures (29 ± 2 kJ/mol) [29]. The relaxation of EG in silicalite shows an intermediate behavior. Its activation energy (35 ± 2 kJ/mol) lies between those of EG confined to sodalite and the apparent activation energy (tangent to the VFT temperature dependence) of the bulk liquid. The temperature dependence is Arrhenius-like; hence, it resembles the single molecule relaxation of EG in sodalite.

For a further analysis of the transition from a single molecule relaxation to the liquidlike behavior, it is essential to know more about the arrangement and interaction of the guest molecules in zeolite beta and silicalite. (In sodalite the guest molecules are apart from each other by 0.89 nm; hence, interactions are negligible).

To that end, computer simulations were performed (on a Silicon Graphics workstation using the molecular simulation program Cerius²) modeling a finite zeolite crystal of four unit cells surrounded by vacuum. By “filling” the pores with EG a completely loaded nanoporous host/guest system can be simulated. The resulting mass percentage of guest molecules is 23% for zeolite beta and 16% for silicalite, which corresponds well to the experimental data obtained by weighing: $22.8 \pm 3\%$ for EG in zeolite beta and $18.2 \pm 2\%$ for silicalite. In conclusion, the simulations describe the host/guest system satisfactorily.

The simulations were carried out using three different force fields: the *Dreiding* force field, which is an all-purpose force field [30], the *Burchart-universal* force field, which is suitable for the treatment of organic molecules in zeolites [31,32], and the *consistent force field* cff 91, which has been applied successfully to study guest molecules in sodalite cages [33]. The three force fields provide the same results within statistical uncertainty. In sodalite [Fig. 3(a)], each cage is occupied by exactly *one* molecule. In silicalite [Fig. 3(b)], the molecules are aligned almost single file along the channels. Figure 3c shows that, in zeolite beta, two EG molecules are located

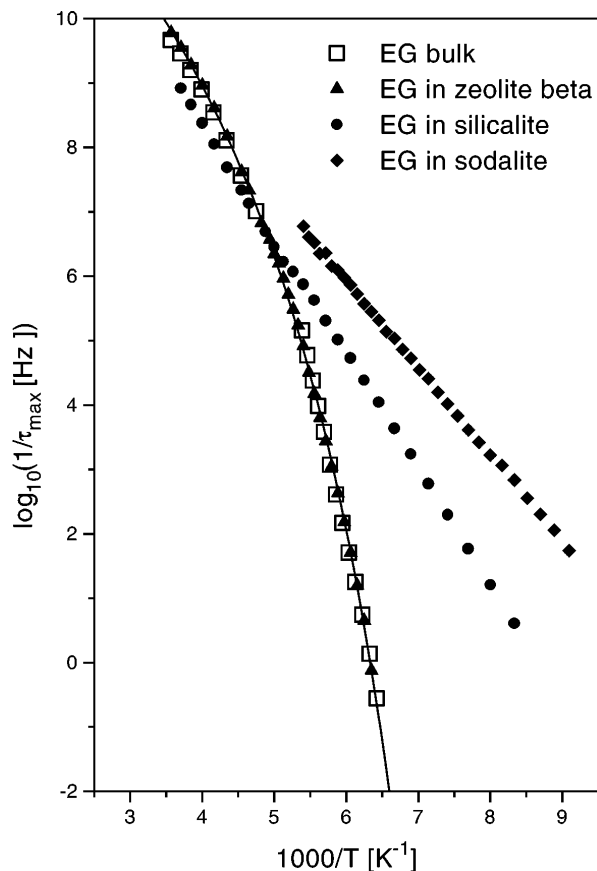


FIG. 2. Activation plot (relaxation rate versus inverse temperature) for ethylene glycol (EG) as a bulk liquid (squares) and confined in sodalite (diamonds), in silicalite (circles), and in zeolite beta (triangles). The errors are smaller than the size of the symbols. The solid line represents a VFT fit according to Eq. (2) for EG confined in zeolite beta. Fit parameters are prefactor $A = 6.8 \times 10^{13}$ Hz, fragility parameter $D = -14.8$, and Vogel temperature $T_0 = 107.8$ K.

side by side in those channels with an elliptical cross section of $0.76 \text{ nm} \times 0.64 \text{ nm}$. The second type of channels (diameter 0.55 nm) is occupied only by a minority ($<3\%$) of the molecules.

The simulation of the molecules in the bulk liquid and in confining space permits a determination of structural parameters of the molecular arrangement (Table I). No significant differences between the bulk and the restricting geometry are found concerning the distance between molecules, the average length of hydrogen bonds, and the density. However, for the number of neighboring molecules (coordination number), a pronounced difference is found (Fig. 4): Within a radius of $r = 0.66 \text{ nm}$ a coordination number of 11 ± 1 is found for the bulk liquid, which corresponds to the maximum value in the case of the random close packing model [34]. Ethylene glycol in zeolite beta has only five neighboring molecules; hence, one has to conclude that an ensemble as small as six molecules is sufficient to perform liquidlike dynamics. Further reduction in the channel size (as in the case

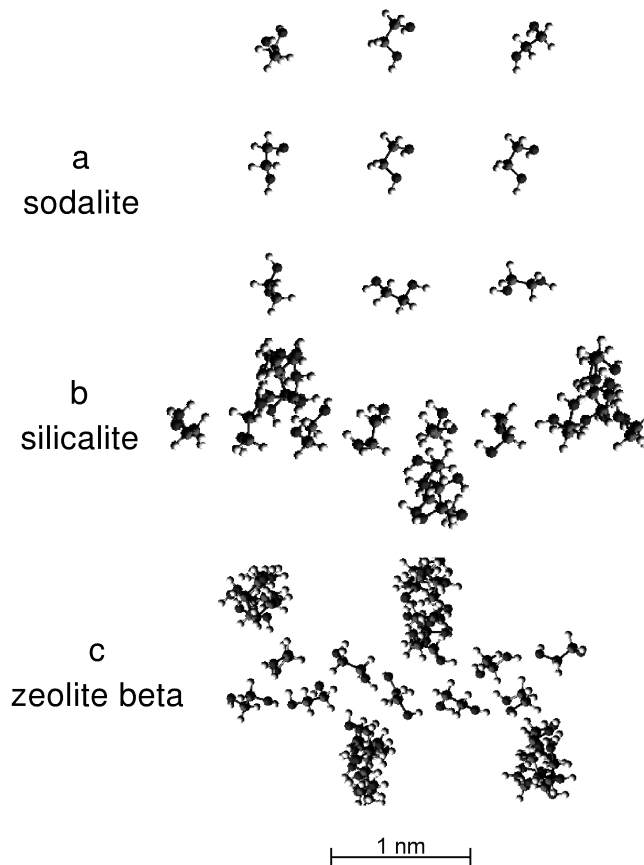


FIG. 3. Results of computer simulations on the arrangement of ethylene glycol molecules confined in zeolites. For better visibility the framework of the zeolites is omitted. (a) sodalite, (b) silicalite, and (c) zeolite beta. The orientation has been chosen for (b) and (c) so that one of the channels runs along the horizontal direction of the paper plane. In adjacent channels perpendicular to the paper plane, the molecules appear as stacked on top of each other.

of silicalite) decreases the average number of neighboring molecules by about 1. This results in a sharp transition from liquidlike dynamics to that of single molecules.

TABLE I. Distance between molecules, average length of hydrogen bonds (O-H...O bonds with a length up to 0.3 nm), and density as calculated from the molecular simulations for ethylene glycol confined to zeolite beta and silicalite and for the bulk liquid. For a simulation of the bulk liquid a limited volume (6.64 nm^3) was filled with EG molecules until the bulk density of 1.113 g/cm^3 was reached. In contrast, the densities of EG confined in zeolites are results of the simulation. The error is mainly caused by the uncertainty in calculating the accessible volume of the zeolitic channels.

	Distance between molecules (nm)	Average length of H-bonds (nm)	Density (g/cm^3)
Bulk liquid	0.42 ± 0.01	0.23 ± 0.02	1.113
Zeolite beta	0.41 ± 0.01	0.25 ± 0.02	1.0 ± 0.1
Silicalite	0.42 ± 0.01	0.24 ± 0.02	1.0 ± 0.1

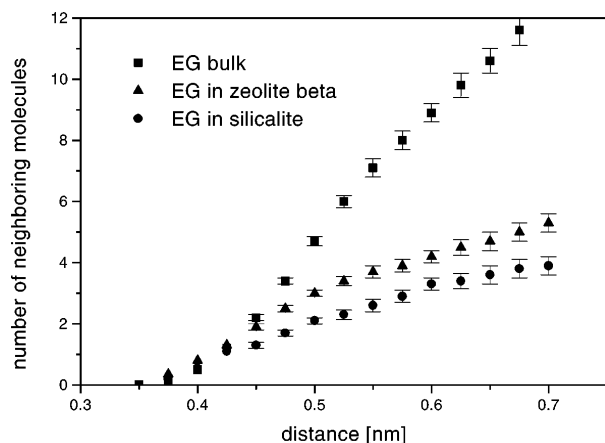


FIG. 4. Average number of neighboring molecules as a function of the radius of a surrounding sphere as calculated from the simulation for EG bulk liquid (squares), EG confined in zeolite beta (triangles), and confined in silicalite (circles). If no error bars are indicated, the error is smaller than the size of the symbols.

The transition in the dynamics of an isolated molecule to that of a liquid state has been measured by broadband dielectric spectroscopy (10^{-2} – 10^9 Hz) and analyzed based on computer simulations. While EG in sodalite (one isolated molecule per cage) shows a single molecule relaxation, one finds for EG in zeolite beta a temperature dependence of the mean relaxation rate which is characteristic for the bulk liquid state. Computer simulations show that an ensemble as small as six molecules is already sufficient to perform liquidlike dynamics.

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*Author to whom correspondence should be addressed.

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