Structure and Dynamics of Zeolites Investigated by Molecular Dynamics

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Contents

I. Introduction

Among the materials which are of interest for chemical science and technology, zeolites are oustanding for their special characteristics and multifarious and widespread uses. Their name was coined by a Swedish chemist and mineralogist, Axel Fredrick Cronstedt (1722−1765), who reported in a short paper the discovery of that subclass of tectosilicates,[1] and was derived from the Greek words $\zeta\epsilon\iota\nu$ and $\lambda\iota\vartheta o\varsigma$ ("boiling stones", because "in the blowpipe-flame they emit gas and puff up", as Cronstedt wrote). The paper appeared in 1756 in the Proceedings from the Swedish Academy of Sciences and it is reported, along with its English translation and some comments, in ref 2. Natural zeolites[3] are found as fine crystals of hydrothermal genesis, in geodes and fissures of eruptive rocks, or as microcrystalline masses of sedimentary origin. They attracted the attention of many researchers 70 years ago, for their unique physicochemical properties, and it was discovered that they could be easily synthesized from aqueous solutions of inorganic salts and organic molecules which act as templates, giving rise to a variety of complex porous crystalline aluminosilicates. Their chemical composition usually consists of silicon, aluminum, oxygen, and exchangeable cations. The crystalline framework is built up by corner-sharing TO_4 tetrahedra (in which the T-sites are occupied by either silicon or aluminum) giving rise to a rather complex but precisely repetitive atomic network with regular cavities joined by channels in which guest molecules of appropriate size can accommodate. These void interior spaces can admit water, many gases, larger molecules, and metallic cations which compensate for the charge deficit due to the aluminum/silicon substitution and can be substituted by ion exchange with metallic cations of different species, including transition metals, protons, or small organic cations. Certain positions on the inner walls of the micropores appear to behave as active sites, where catalytic conversions can take place. Selectivity can be obtained by adjusting the size of the micropores or cavities and by modifying the location of the active sites in such a way that, ideally, only one type of molecular species can reach these active sites. This is achieved using different framework topologies; therefore, there is a constant demand to discover new zeolite structures and their relationships to the ones already known. Indeed, the use of zeolites in industry and other fields of economical interest is widespread and diverse: they are employed as catalysts and molecular sieves in chemical industry; as ion exchangers, in particular for the treatement of waste water; and as absorbents in detergents; they are used in animal nutrition and aquacultural farms,[4] and some applications in microelectronics[5] as well as for hydrogen storage[6] have been proposed. Therefore it is very important to understand the relation between the structure of a zeolite and the adsorption and fate of specific molecules. It would be highly desiderable to develop theoretical methods for predicting zeolite behavior, to facilitate selection and optimization of zeolites for a given purpose. However, as of yet no satisfactory theory of adsorption and transport in zeolites has been proposed, and even the detailed description of the main chemical processes occurring in zeolites escapes understanding and rationalization. In most phenomena occurring to molecules in zeolites, diffusion plays an essential role, *e.g.*, it favors absorption, makes separation of similar molecules effective, and drives chemical reactions both on the reagent side to lead the reactants into the active sites and on product side to select and extract the species resulting from the reaction. On the other hand, diffusion is a "mechanical" phenomenon, and its computer simulation using different techniques has become feasible in the last decade, making it possible to study the details of the diffusive processes of simple molecules adsorbed in the micropores of zeolites and the influence of the framework structure and dynamics

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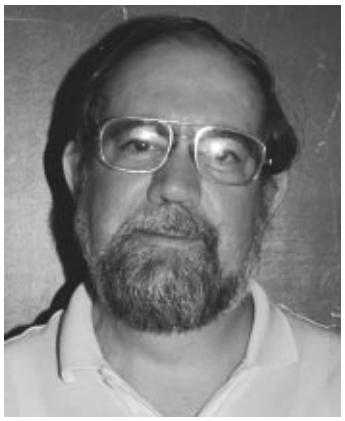
Pierfranco Demontis was born in Sassari, Italy, in 1954. He received his degree (Laurea) in chemistry from the University of Sassari in 1979. After postoctoral work at the same university under the supervision of Professor A. Gamba (1979–1983) he entered the University of Sassari as researcher in 1983, and since 1992, he as been working there as an Associate Professor of Physical Chemistry. In 1987–1988 he spent one year working as Postdoctoral Fellow at the University of Pennsylvania with Professor M. L. Klein. His main scientific interest is on applying computer-simulation techniques to study adsorption and diffusion in zeolites.



Giuseppe B. Suffritti was born in Genova, Italy, in 1947. In 1972 he received his degree (Laurea) in physics from the University of Milano and worked at the same university for four years, collaborating with the group of Professors Massimo Simonetta and Carlo M. Gramaccioli studying the lattice dynamics of molecular crystals. He spent one year (1974) in Paris, France, at CECAM, developing programs for lattice dynamics calculations. In 1976 moved to the University of Sassari, where he became lecturer of Physics and Physical Chemistry, and since 1983, he has been working there as an Associate Professor of Physical Chemistry. His scientific interests span a wide range, always in the field of computational and theoretical chemical physics. He developed computational codes for performing lattice dynamics calculations on molecular crystals. Collaborating with Professor Aldo Gamba, he carried out investigations on the solvent effect in chemical reactions with quantum mechanical computational methods and on the solvation of small molecules in water using the Monte Carlo procedure and deriving from quantum mechanical calculations the suitable intermolecular potentials. Since 1983, his current research interest is on the application of molecular dynamics simulations to liquids and solids, and in particular to zeolites and related microporous materials. He developed, in collaboration with Professor Demontis at the University of Sassari, flexible codes for molecular dynamics simulations of zeolites. Present collaborations of the group in Sassari involve Professors R. Haberlandt, J. Kärger, and S. Fritzsche at University of Leipzig, Leipzig, Germany, and Dr. Yashonath at the Indian Institute of Science, in Bangalore, India.

on diffusion and to approach investigations on simple chemical reactions. In this review, we will restrict our interest to molecular dynamics (MD) simulation of zeolites. Our goal is to illustrate this powerful technique and outline results and problems in its application to these complex systems. We shall not follow a chronological order, because the studies in this field are devoted to different phenomena occurring in zeolites, which will be treated separately. The basic features of the MD simulation technique are illustrated first. The application to zeolites of closely related simulation techniques like the Monte Carlo (MC) method (refs 7−11 are recent examples) will not be treated, because the review would become cumbersome and too complex, and we do not feel sufficiently involved in this field.

II. The Molecular Dynamics Simulation Technique

When modern computers became available for the scientific community, new powerful tools for verifying theoretical results and for simulating complex phenomena in the condensed matter field were on hand, and the era of the "computer experiments" rose up. In particular, the MD technique was developed by Alder and Wainwright[12] in 1957 in order to simulate the behavior of hard spheres in a box depending on temperature and density, a field of current investigation at that time among statistical mechanics specialists. MD[12−15] is a method for studying the microscopic behavior of well-defined systems of particles through the solution of classical equation of motion. Newton, Hamilton, or Lagrange equations are used, depending on the characteristics of the system and the computer code optimization. When applied to atomic or molecular sytems, MD is used as an approximation of the more exact but much more complex and computationally demanding quantum mechanical calculations. Detailed descriptions of this technique can be found in the book by Allen and Tildesley[13] (for recent developments, see ref 14), and most applications to the field of zeolites are reported in ref 15. We will outline here the main features of MD only, but new and special tools for the study of zeolites will be illustrated in more details. In order to perform MD simulations of a system, a set of N classical particles characterized by coordinates, velocities, and masses is chosen. The particles usually interact through a potential which, in most investigations, is taken to be the sum of suitable pair potentials, depending on the distances between particles, but more sophisticated models are sometimes used. The forces acting on the particles are evaluated from the derivatives of the potentials, and the equations of motion are solved numerically by standard methods. As the system evolves in time, it eventually reaches equilibrium conditions in its structural and dynamical properties. The statistical averages of interest are calculated from the positions and the velocities of the particles as time averages over the trajectories of the system in its phase space. Spectral densities and simulated IR spectra can also be derived from time evolution of the system.[15] For practical reasons (mainly available computer storage and time), the number of particles is restricted to at most a few thousands, and in order to avoid surface effects, to simulate bulk systems periodic boundary conditions are commonly used. These are obtained by repeating a unit cell of volume V containing the N particles by suitable translations, so that the same number of particles is contained in a cell of the same

volume. The statistical mechanical ensemble which is generated by the usual MD simulations is the microcanonical or NVE ensemble, where the number of particles, volume, and total energy are constant, but it is possible, by using special techniques,[16] to simulate a canonical or NVT ensemble, where a thermal reservoir is added to the system, or the isobaric−isothermal ensemble (NPT), where pressure and temperature are held constant by some suitable algorithm like the Parrinello and Rahman scheme[17−19] and the cell parameters are allowed to change accordingly. In connection with this topic, some interesting problems arise when performing MD simulations of zeolites. In the zeolitic systems, at least two distinct subsystems can be found: (i) the aluminosilicate framework, which under usual conditions does not change its connectivity but can vibrate and may be deformed by external strains or by the occluded molecules, (ii) the sorbate particles subsystem, including, sometimes, the cations present in the channels and cavities in the framework.

When the interest is focused on the behavior of the occluded species, the framework is often kept fixed. This approximation may be reasonable for some systems, especially at low temperatures, and avoids both the difficult problem of elaborating a good model potential for the framework and the need for large computational labor. However, a fixed framework approximation entails a fixed volume for the system, and the usual experimental conditions for zeolites, corresponding to the isobaric−isothermal ensemble (NPT), cannot be reproduced exactly. On the contrary, the only ensemble which can be simulated, besides the microcanonical ensemble is (for the sorbate subsystem) the canonical one (NVT). This can be performed by using the above mentioned special MD techniques, but an alternative way is to apply a naive harmonic model for the motion of the framework,[20] which turned out to provide a good heat bath for the sorbate molecules without requiring a large computational effort and performing calculations in the usual NVE ensemble for the whole system. As this model can yield a reasonable reproduction of the vibrational frequencies and amplitudes of the framework, the collisions and the deformations of the framework experienced by the sorbate molecules are fairly realistic. Indeed, it is able to reproduce, at least with a fair approximation, the deformations of the framework which can become critical, for instance, when the breathing motion of the windows connecting adjacent cavities influences the diffusivity of guest molecules whose dimensions fit the window opening. NVT simulations would completely neglect this phenomenon. MD is a relatively simple simulation technique and usually does not require special computer resources. The major technical problems associated with the simulation of zeolites are possibly the choice of the potential models, which derives from the approximations which are adopted to describe the systems. They depend obviously on the phenomena and quantities which one wants to study. For instance, a qualitative understanding of diffusive processes can be obtained from a simplified model where the guest molecules are rigid or are represented by soft spheres, but quantitative reproduction of diffusion coefficients of flexible molecules or the description of chemical reaction mechanisms would require more and more sophisticated models. A good knowledge of the basic crystallography and solid state physics as well as the principles of the liquid state science could help in designing the system to be simulated and to interpret the results, taking into account the tools of statistical mechanics. Many technical details can be found in refs 13−19. To our knowledge, the first application of MD simulation technique to zeolites was published in 1986.[21] It was a study of the behavior of flexible water molecules in natrolite, a natural zeolite (See section III.B.3), and was followed by a few papers in 1987 and 1988. In 1989, after the 8th International Zeolite Conference held in Amsterdam, where the results of some MD studies on zeolite were illustrated, this technique attracted the attention of several research groups all over the world and the interest as well the number of the published papers increased. This review should cover in principle all the literature published until the end of 1996 on the application of the MD technique to zeolites, but some papers of minor relevance or those that appeared in small journals could have escaped our investigation.

A. Structural Properties

The raw product of a MD simulation is a sampling of the phase space accessible to the system, *i.e.*, the set of the positions and linear momenta (masses times velocities) of the particles belonging to the system in a given time interval, starting from given initial conditions. Therefore, statistical tools are used to derive the quantities that can be compared with the corresponding experimental ones or, more generally, that can be useful for the detailed study of the system. While most of these tools are well-known and standard for fluids, special ones have been developed for zeolites. From the subset of positions it is possible to extract, among the others, structural information concerning both the framework atoms (including the charge-compensating cations, when they do not diffuse) and the sorbed species. In the framework, the atoms usually vibrate around equilibrium positions, and hence their mean coordinates (as time averages of the instanteneous coordinates throughout a simulation) and the distributions of these coordinates (as frequency histograms for the values of the coordinates around their mean) can be easily computed. However, because zeolitic structures usually show some (and often high) degree of symmetry, the list of the mean coordinates is scarcely useful for a comparison with experimental data, and the distribution functions will appear mostly Gaussian-like, giving no significant structural information. A procedure which allows a direct comparison with the diffraction experiments and yields suggestions about the symmetry group to which the simulated system could fit was developed by Demontis *et al.*[20] At each step, the coordinates of the atoms of the framework are referred to the asymmetric unit of the crystal by the inverse operations of a selected symmetry group (usually the experimental one, if any) and accumulated in histograms in order to evaluate their distribution functions, which correspond to the

superimpositions of the distribution functions coming from all the atoms related by symmetry to a particular atom. The mean coordinates of the atoms in the asymmetric unit are then evaluated from their distributions following the standard statistical procedures, but the shape of the single coordinate distributions yields useful information for the structural analysis of the simulated crystal. Indeed, when the atoms vibrate about positions which are consistent with the given symmetry group, the superimposed distribution functions of their coordinates are Gaussian-like, and their half-width is similar to that of a distribution function of an atom. If the simulated crystal is ordered, but its symmetry group is different from the given one, the distribution functions of the coordinates will appear bimodal (split) or multimodal. In general the splittings are different for different atoms; if they are equal for all atoms, it means that a rigid translation of a portion of the simulated crystal occurred, and a "domain structure" (*e.g.*, a twinning) was generated. Very large or irregular distribution functions may arise from disorder, and diffusion processes are shown by flat distributions. This kind of analysis can be repeated for different symmetry groups, until the best consistency is reached, if the coordinates are stored. A similar procedure can be used for bond distances and angles and their distributions, both for the solid-like subsystem and for structured sorbed molecules. Because of the correlation of atomic motion, these quantities in general are different from the same quantities obtained directly from mean atomic positions and their distributions and must be computed separately. For the diffusing species subsystem some statistical tools that are usually adopted for the structural analysis of liquids can be exploited. Most of them are related to the pair distribution functions and give the probability of finding a pair of atoms at a distance apart, relative to the probability expected for a completely random distribution at the same density. Pair distribution functions can be evaluated from MD simulations by frequency histograms. The structural information that can be derived from these distribution functions are, for instance, the mean distances between sorbate particles and between these species and the framework surface, as well as the coordination of the cations by sorbate molecules. Two examples of radial ditribution funtions are reported in Figures 1 and 2. In Figure 1 the distribution of the center of mass of methane−oxygen atoms of the framework in the cages of dealuminated zeolite A (see section 3.A.II) is plotted for three different loadings. The trend toward the structuring of the confined fluid as the number of the guest molecules is increased is evidenced by the more and more pronounced oscillations of the function. This trend is confirmed in Figure 2 by the corresponding distribution functions of methane−methane center of mass. Other special distribution functions have been used for the analysis of MD simulations of zeolites, *e.g.*, density distributions functions of sorbed molecules along the axis of a channel, in a slice of the system box, or in the whole volume which is accessible to the sorbate molecules. These last distributions are illustrated by using volume rendering graphics or contour level plots for selected planes cutting the channel or the cavities. The last case is illustrated in Figure 3, where the contour plot of the density distribution function of the center of mass of methane molecules in dealuminated zeolite A (see section 3.A.II) is reported for the equatorial plane of the nearly spherical cages of this zeolite. It appears that the sorbed molecules avoid visiting the center of the cage and remain close to the surface, crowding in preferred positions which are located just in front of the windows connecting the cage with the adjacent ones. Another example is shown in Figure 4 for the distribution of the center of mass of ethane molecules in silicalite in two different channel intersecting systems (see sections 3.A.I and 3.B.I). It appears that the adsorbed molecules preferentially avoid intersections and spend most of the time in the channels,

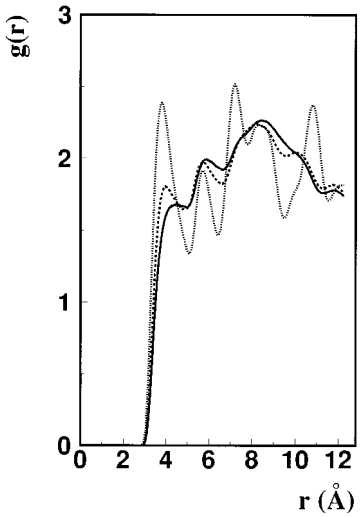


Figure 1. Pair distribution functions of the center of mass of methane−oxygen atoms of the framework in the cages of dealuminated zeolite A (see section 3.A.II) for three different loadings at 357 K: continuous line, 1 molecule per α-cage; dashed line, 7 molecules per α-cage; and dotted line, 15 molecules per α-cage. (Data from ref 247.)

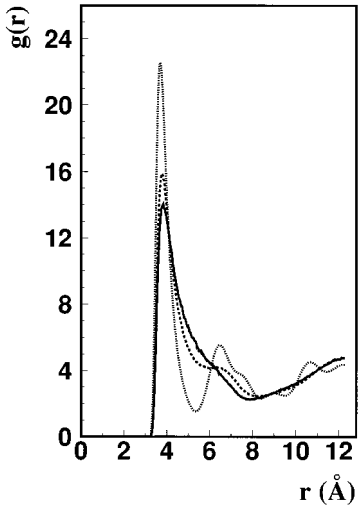


Figure 2. Pair distribution functions of the center of mass of methane−center of mass of methane in the cages of dealuminated zeolite A (see section 3.A.II) for three different loadings at 357 K: continuous line, 1 molecule per α-cage; dashed line, 7 molecules per α-cage; and dotted line, 15 molecules per α-cage. (Data from ref 247.)

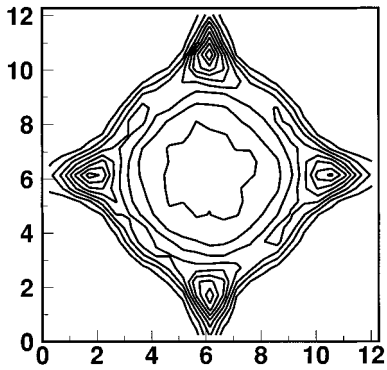


Figure 3. Contour plot of the density distribution function of the center of mass of methane molecules in dealuminated zeolite A (see section 3.A.II) for the equatorial plane of the nearly spherical cages of this zeolite at 357 K. The loading is one molecule per α-cage. The four peaks correspond to positions just in front of the windows connecting adjacent cages. Distances are in angstroms. (Data from ref 65.)

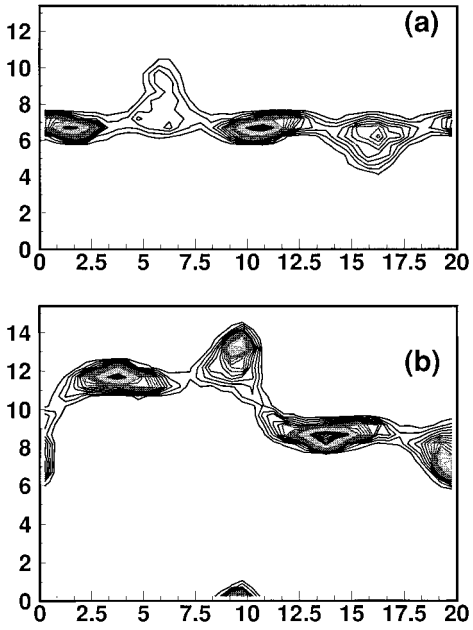


Figure 4. Contour plot of the density distribution function of the center of mass of ethane molecules in silicalite (see sections 3.A.I and 3.B.I) at 300 K: (a) for the axial plane of the straight channel system and (b) for the axial plane of the sinusolidal channel system. The loading is eight molecules per unit cell. Distances are in angstroms. (Data from the simulation reported in ref 50.)

suggesting a diffusive process by "jumps" (see section 3.A.I). Other interesting quantities which are related to the coordinates and which are in part of dynamical nature are the structure factors. Their evaluation is described in detail in ref 15, but they are only mentioned here because, though they could be easily derived from MD simulations for a direct comparison with X-ray and neutron diffraction and inelastic scattering experiments, they are seldom found in papers published so far. Further analyses can be performed using coordinates. One example is the study of the nature and duration of dimers and clusters of sorbate molecules. If a clear-cut definition of a molecular dimer is available (*i.e.*, a dimer is present if the molecules remain closer than a certain distance d_o) it is easy to evaluate the distribution functions of the duration of the dimers and to derive their mean lifetime. This could be interesting, for instance, if the "encounters" between molecules could be reactive. This kind of analysis can be extended to clusters of any number of molecules. If the distance d_o between the molecules corresponds to a repulsive intermolecular energy $E(d_o)$, the same analysis yields the number and the duration of binary and multiple collisions between molecules of energy higher than $E(d_o)$. This information are useful to study for instance the probability of a chemical reactions showing an energy threshold. Similar studies can be performed on temporary complexes and on collisions between the framework atoms and the sorbed species. Finally, by monitoring and averaging the time spent by a sorbate molecule in a cavity or in a channel portion, the average residence time in these space regions can be estimated and this quantity can be useful for the discussion of the long-range diffusion mechanisms in zeolites.

B. Dynamical Properties

From the subset of velocities in the phase space portion which is explored by the MD simulations, a number of dynamical properties of the system can be obtained. Some of them are average quantities, like the mean kinetic energy or the diffusion coefficients, while some others are time dependent properties. In classical statistical mechanics the simulated temperature of a system is proportional to the mean kinetic energy, but the mean square fluctuation of the temperature, $\sigma^2(T)$, is different for different ensembles. It is always proportional to the inverse of the number of particles of the system, so that it is relatively small for systems containing some hundreds of atoms (typically, a zeolite unit cell) but may be large for the sorbed molecules subsystem. Moreover, for a canonical ensemble $\sigma^2(T)$ is proportional to the square temperature, while for a microcanonical ensemble it is smaller, as the square temperature is multiplied by a factor less than one (see, *e.g.*, ref 15), so it can be used, for instance, as a statistical tool to evaluate the effectiveness of the framework as a heat bath for the sorbate molecules subsystem. The pressure of a simulated system can be obtained from the temperature T and the internal virial W by the well-known equation[15]

$$PV = Nk_BT + W \tag{1}$$

where V is the volume, k_B is Boltzmann's constant, and N is the number of particles of the system. Unfortunately, eq 1 contains the volume and can be used for the whole simulated system but not for the sorbate subsystem, because its effective volume is not well-defined and it depends on temperature. Most of the time dependent properties can be obtained in terms of correlation functions. A non-normalized time correlation function is defined, for two time-dependent quantities, $f(t)$ and $g(t)$, as follows

$$C_{fg}(t) = \langle \delta f(t)\, \delta g(t) \rangle \tag{2}$$

where $\delta f(t) = f(t) - \langle f \rangle$; $\delta g(t) = g(t) - \langle g \rangle$. The brackets mean time averages over the sampled region of the phase space. The meaning of t in eq 2 is that of the final and initial time of an interval of duration t, and

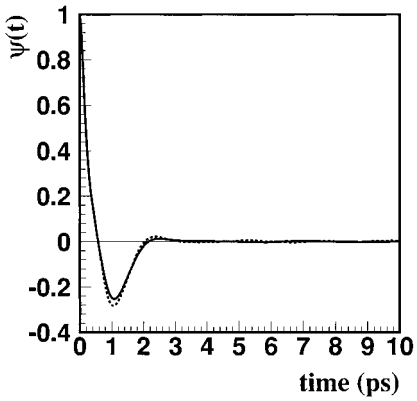


Figure 5. Velocity autocorrelation function of the center of mass of methane molecules in dealuminated zeolite A (see section 3.A.II) at 357 K. The loading is one molecule per α-cage: continuous line, simulation with flexible framework model; and dashed line, simulation with fixed framework model. (Data from ref 113.)

the average might be taken over the largest number of time intervals available with statistically independent initial time in a simulation. In order to obtain a good statistical evaluation of a time correlation function, usually the maximum value of the time interval considered is less or equal to one-half of the duration of the simulation. If f and g are the same quantity, then the time correlation function is called the time autocorrelation function (vacf). In particular, the inspection of the velocity autocorrelation function can yield interesting information about the dynamical behavior of the sorbed species. For instance, from the time when it becomes negative, the average time between collisions may be estimated and, more generally, the dynamical behavior of the sorbate molecules in a short time scale can be discussed. One example consisting of the autocorrelation functions of the center of mass of methane molecules in dealuminated zeolite A (see section 3.A.II) is reported in Figure 5 for two simulations based on different models of the framework. The one represented by a dotted line, which is sharper, is obtained by keeping the framework fixed. The smoother continuous line results from a simulation where the framework is flexible and thus the collisions with the guest molecules cause a softer backscattering. Moreover, the velocity autocorrelation function, according to the linear response theory, is related to the diffusion coefficient D by

$$D = \frac{1}{3}\int \langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle \, \mathrm{d}t \tag{3}$$

and the Fourier transform of the velocity autocorrelation function yields the power spectrum of the system, which corresponds to the vibrational analysis that can be performed experimentally by inelastic neutron scattering (INS). Infrared (IR) and Raman spectra can be simulated, with some approximations, using the classical linear response theory,[15,22−29] by the Fourier transform of the autocorrelation function of the total dipole moment of the system and of the polarizability tensor of the system, respectively. These quantities must be estimated at each time step in the MD simulation, most usually from an explicit dependence of the two quantities from coordinates, which can be derived by using the results of quantum mechanical calculations or can be assigned on empirical grounds. For instance, in the case of IR spectra it is sufficient to assign a reasonable electric charge to the atoms of the system and to compute the dipole moment from the instantaneous charge distribution. Care must be taken in the numerical evaluation of the Fourier transform, because finite time simulations generate unphysical extra frequencies in the spectrum, and special numerical techniques such as windowing[29] must be employed. Moreover, because of the finite size of the system, the raw simulated frequency spectrum is not continuous, even if the spectra are computed as averages of a number of independent simulations, and many close together lines appear instead of a band as in experimental spectra. In order to make the comparison with experiment easier, the computed spectra can be smoothed by subtituting the intensity for a given frequency with the average of the intensities for a few contiguous frequencies.[30] More remarks and examples of simulated spectra are reported in section II.D below. Finally, the transport coefficients can be evaluated by using, instead of eq 3, the well-known Einstein formula

$$D = \lim_{t\to\infty} \frac{\langle \Delta r^2 \rangle}{6t} \tag{4}$$

where $\langle \Delta r^2 \rangle$ is the mean square displacement of the particles avaraged on trajectories of duration t. As pointed out by Fritzsche *et al.*,[31] other statistical mechanical formula can be adopted to derive the diffusion coefficient

$$D = \lim_{t\to\infty} \frac{\pi(\langle |\Delta r| \rangle)^2}{16t} \tag{5}$$

$$D = \lim_{t\to\infty} \frac{16(\langle |\Delta r|^3 \rangle)^{2/3}}{(4\pi)^{1/3}t} \tag{6}$$

$$D = \lim_{t\to\infty} \frac{(\langle \Delta r^4 \rangle)^{1/2}}{(60)^{1/2}t} \tag{7}$$

and the convergence of the estimates of D obtained from the above eqs 4−7 toward a well-defined value may be a good test for the statistical consistency of the simulation. These equations hold for long-range diffusion occurring in a relatively long time scale and state that on that scale the mean square displacement $\langle \Delta r^2 \rangle$ is linear with time. One example of the trend of $\langle \Delta r^2 \rangle$ *vs* time is reported in Figures 6 and 7 for two different time scales and describe the behavior of methane molecules in dealuminated zeolite A (see section 3.A.II). As in Figure 5, the dashed lines describe the behavior of $\langle \Delta r^2 \rangle$ as obtained from a simulation where the framework is kept fixed, while the continuous lines are related to a flexible framework model. Figure 6 shows that for very short times (less than 1 ps) the two curves are close together, as they correspond to the motion of the guest molecules within one cage, while they diverge for times allowing long-range (intercage) diffusion, as the breathing motion of the windows connecting the cages favors

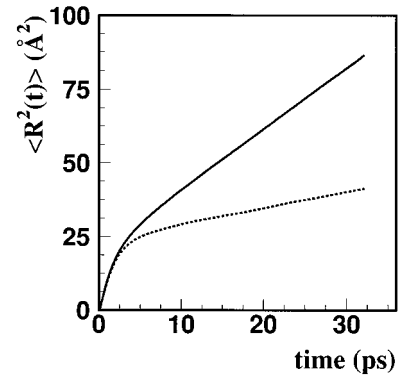


Figure 6. Mean square displacement $\langle \Delta r^2 \rangle$ of the center of mass of methane molecules in dealuminated zeolite A (see section 3.A.II) at 357 K for short times. The loading is one molecule per α-cage: continuous line, simulation with flexible framework model; and dashed line, simulation with fixed framework model. (Data from ref 113.)

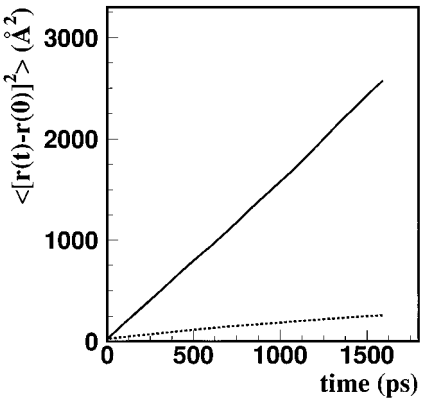


Figure 7. Mean square displacement $\langle \Delta r^2 \rangle$ of the center of mass of methane molecules in dealuminated zeolite A (see section 3.A.II) at 357 K for long times. The loading is one molecule per α-cage: continuous line, simulation with flexible framework model; and dashed line, simulation with fixed framework model. (Data from ref 113.)

the outflow of the guest molecules (see also section 3.A.II). In Figure 7 it is demonstrated that the computed $\langle \Delta r^2 \rangle$ in both cases remains remarkably linear also for larger time scales (the trajectories lasted about 6000 ps). Interesting phenomena like oscillations, intracavity diffusion, *etc.*, whose characteristic time scale is relatively small may be investigated, besides by inspecting velocity autocorrelation functions, by using log−log plots. By plotting log ($\langle \Delta r^2 \rangle$) *vs* log($t$) on a logarithmic scale, every linear region of the resulting plot denotes a distinct diffusive regime, represented by a power law like $D = At^a$; *e.g.*, the Einstein diffusive regime is described by a straight line of slope 1. Therefore, it is possible to obtain the characteristic time and space length of every regime and to draw some conclusions about the diffusion mechanism. Usually there are at least three distinct regimes: for very short times on the order of $^1/_{10}$ of ps, the straight line has slope 2, corresponding to Newtonian dynamics (nearly free motion) $\langle \Delta r^2 \rangle = ut^2$; in the long time limit the straight line has slope 1, corresponding to Einsteinian regime $\langle \Delta r^2 \rangle = 6Dt$; and, finally, the intermediate times show a more or less complex behavior including, in different situations, jumps and oscillations. It is important to remark that, when evaluating $\langle \Delta r^2 \rangle$ for long time intervals, Δr may become larger than the MD simulation box side; therefore, in this calculation the coordinates must be evaluated without reducing them to the original box (as is done usually for MD simulations of liquids), but if a particle crosses the box wall its position must be ascribed to an adjacent box, and it must not be reported to the original box by subtracting a box side length. This procedure is possible in zeolites because the framework possesses a translational crystallographic symmetry and the particle which crosses a box wall finds an environment which is identical to the box which it leaves not only in the simulated but also in the real system. Experiments show that usually the diffusion of sorbed species in the micropores of a zeolite is an activated process, *i.e.*, it follows the Arrhenius equation

$$D = D_o \exp(-E_a/RT) \tag{8}$$

where E_a is the activation energy, R is the gas constant, and T is the temperature. By computing the diffusion coefficients for simulations at different temperatures and fitting them to an Arrhenius plot (log D *vs* $1/T$) it possible to evaluate the simulated activation energy and to compare it with the experimental results. The above formulae (4−8) hold for homogeneous and isotropic fluids at equilibrium, but zeolites are not a homogeneous nor an isotropic medium for the diffusing sorbed molecules. However, because most of experimental measurements are performed using aggregates of randomly oriented crystallites, eqs (4−8) can be used also for zeolites, allowing a direct comparison between experimental and computed data. In the theory of diffusion in anisotropic media, the diffusion coefficient D is replaced by a 3×3 diffusion tensor whose principal axes are related to diffusion directions about which symmetry is present. Diffusion along the axis of a channel can be described as a monodimensional process, characterized by a monodimensional diffusion coefficient, which sometimes has been estimated from special experimental settings and can be evaluated from MD simulations using the formula

$$D_x = \lim_{t\to\infty} \frac{\langle \Delta x^2 \rangle}{2t} \tag{9}$$

where $\langle \Delta x^2 \rangle$ is the mean square displacement along the direction x. Monodimensional diffusion coefficients are also important because, by performing MD simulations at different temperatures, their Arrhenius plot yields an estimate of the activation energy of the diffusive process along a given direction. The diffusion along a channel sufficiently narrow to prevent the guest molecules to pass one another may be modeled as the dynamics of a single-file system, a field which recently received some attention just in connection with zeolites both from the statistical mechanical and MD simulation viewpoint (see, *e.g.*, refs 32 and 33). For a single-file system moving along an axis x, the Einstein formula (4) must be replaced by a relation of the type

$$F = \lim_{t\to\infty} \frac{\langle \Delta x^2 \rangle}{2(t)^{1/2}} \tag{10}$$

where the factor of proportionality F has been termed the mobility factor of single-file diffusion, and it is related to the infinite dilution diffusion coefficient along x, D_{id}, the one-dimensional density, $\rho = 1/l$ (where l is the average distance between molecules), and the length of the molecule along x, σ, by

$$F = \frac{(1 - \rho\sigma)}{\rho}(D_{\mathrm{id}}/\pi)^{1/2} \qquad (11)$$

Hahn and Kärger investigated in a recent paper (ref 32) the behavior of different model systems and they concluded that only if the motion of the particles is completely uncorrelated with the initial velocity is eq 10 well-reproduced by MD simulations. This is achieved by including random forces explicitely or via a periodic potential helping the particles lose the memory of the initial velocity. A recent investigation of this kind of diffusion in zeolites (ref 33) will be illustrated below (section III.A.3).

C. Activated Processes

In the previous section it was recalled that usually diffusion is an activated process, *i.e.*, to occur it requires overcoming an energy barrier. Other activated processes are found in zeolites, the commonest examples being the adsorption of a molecule which from a gas or a liquid enters into the micropores and, especially, chemical reactions occurring in the channel and cavities. If the activation energy is smaller than, equal to, or slightly larger than the available thermal energy $k_B T$, the probability of overcoming the energy barrier is sufficiently high to allow the activated process to occur for a statistically meaningful number of times during a reasonably long simulation. Otherwise, the activated process becomes a collection of "rare events" and enormous amounts of computer resources can be wasted without detecting one of these events using ordinary MD simulations. Fortunately, special techniques have been designed in order to solve this problem and make it possible to study "rare events" with a reasonable computational effort. This problem is related to the well-known transition state theory (TST), a statistical mechanical approach to the study of chemical reactions and, more generally, to processes having high activation energies.[15,34] For MD simulation of activated processes a method proposed by Keck[35,36] and Anderson[37,38] can be used: the MD trajectory is inizialized from an equilibrium distribution of all variables except the position along the reaction coordinate, which is constrained to the top of the barrier or, more exactly, to the transition state of the process. Starting from these positions, the dynamics of the system is computed without constraints both forward and backward in time, thus determining if the trajectory is successful in crossing the energy barrier, *i.e.*, if the activated process occurred. This technique has been applied for models of solution phase chemical reactions[39−43] and theoretical developments on this topic have been discussed.[44−48] Application to zeolites is illustrated in section V.C below. All these techniques can be considered as examples of nonequilibrium molecular dynamics (NEMD). NEMD includes a series of special extensions of MD simulations where the system is relaxed from a nonequilibrium configuration or it is maintained out of equilibrium by applying an external action (see ref 5 for more details). In the field of zeolites, as will be reported below, NEMD has been applied to study, for instance, the dependence of the diffusivity on the concentration[49] and the relaxation of the vibrational energy of excited sorbed molecules.[50]

D. Classical *vs* Quantum Mechanical Simulations

The use of *classical* mechanics for studying the dynamics of microscopic systems like the ones considered in this paper, where the *quantum* mechanics should be applied, deserve some comments. For translational motion, it is well-known that the classical mechanics yields good approximations of the quantum results, as far as light atoms (like the hydrogen isotopes) are not involved, and this is true for almost all MD simulations of zeolites reported so far. The same arguments hold also for rotations, even if in this case the energy levels are not so close together and, therefore, the approximation is not so good. Nevertheless, classical MD has been used extensively for simulations of molecular fluids, where free and hindered rotations are present, without raising criticisms. All other motions, in systems like zeolites, have a vibrational or oscillatory character. If they are harmonic, the frequencies derived from classical mechanics correspond to the quantum mechanics energy levels so that the vibrational spectra show the same frequency lines or bands, but the intensities may be different, and therefore frequency-dependent corrective factors have been proposed.[26,27] If anharmonic motions are present, some (usually small) corrections should be applied.[26,27] The most difficult problem comes from the comparison of the amplitudes. In classical mechanics, the mean square amplitude of a (harmonic) oscillator is proportional to its kinetic energy or, for a large collection of oscillators, to the temperature of the system and vanishes at 0 K. On the contrary, a quantum oscillator, due to the indetermination principle, at 0 K possesses an energy $E_o = 1/2h\nu$ higher than the minimum of the potential with a mean square amplitude $\langle A^2 \rangle = E_o/k_e$ (where k_e is the elastic constant of the oscillator) and the dependence of $\langle A^2 \rangle$ on temperature becomes linear and close to the classical value for temperatures such that $h\nu \ll k_B T$. Therefore, the values of $\langle A^2 \rangle$ as obtained by following classical mechanics are always *smaller* than the corresponding quantum mechanical ones and MD simulations always underestimate the vibrational amplitudes. The error is on the order of 0.1 Å^2 or smaller at room temperature, but it is not negligible for the instance when the diffusivity of the sorbed molecules depends critically on the pore effective diameter. Another application where quantum mechanics should be used instead of the classical one is the relaxation of the vibrational energy of excited sorbed molecules. The transfer of energy from a vibrationally excited molecule is a quantum phenomenon, being more probable when the energy level gaps of the molecule are equal or larger but close to those of the framework. For harmonic oscillators, the

energy level gaps are proportional to the frequency, and the quantum energy transfer corresponds to the classical resonance between oscillators, where the maximum energy transfer rate occurs when the frequencies of the oscillators are equal. The dependence of the energy transfer rate on frequency is not so different in quantum and in classical mechanics, so even if oscillators in real systems often are not exactly harmonic, from the above considerations it appears reasonable to use classical MD as a guideline for the study of energy transfer phenomena. Another difference between classical and quantum mechanics in modeling microporous materials was recently evidenced by Beenakker *et al.*[51] When the difference between pore diameter and the molecular hard core is no longer large compared to the de Broglie wavelength of radial motion, the zero-point energy of the radially confined particle may overcompensate the attraction of the wall, creating an energy barrier at the entrance of the pore or at the passage through a window connecting adjacent cavities. This discrepancy could be reduced by increasing, in classical simulations, the effective diameter of the sorbed molecules, in order to reproduce experimental data. The increased diameter could also balance, at least in part, the the too large void space left in micropores by the underestimation of the vibration amplitutes of the framework atoms (see above). Therefore, if the potential energy functions used in classical MD simulations to represent host−guest interaction are derived by accurate quantum mechanical calculations, this correction should be taken in account. Finally, some remarks must be devoted to the Car−Parrinello[14,52,53] (CP) method, which is often referred to as first-principles or *ab initio* MD. In the CP method, *classical* equations of motion are applied to an extended system including atomic nuclei and the electronic single particles wavefunctions parameters. The electronic wavefunctions are approximated, within the density functional approach[54] for solids, by using a tridimensional Fourier expansion for valence electrons (so that translational symmetry is built-in for the model and application to crystalline solids is straigthforward). Suitable pseudopotentials are adopted to represent local interactions between valence and core electrons. The equations of motion of the extended system are such that the nuclei move according to the forces derived (*via* the Hellmann−Feynman theorem) from the instantaneous electronic ground state and at the same time the parameters of the electronic wavefunctions evolve remaining always very close to the the ground state defined by the minimum of the energy functional. Therefore, only the forces acting on nuclei are of quantum origin, but their motion follows the classical mechanics rules. The CP method is interesting because it needs no input from experimental data to develop interatomic forces, but it requires large amounts of computer storage and time, so application to zeolites is just beginning (see section IV.C below). In order to overcome the above mentioned problems one could attempt to include quantum effects into classical simulations, and among the techniques which have been proposed is the path integral method,[55−57] as shown by recent applications (see, *e.g.*, refs 58−60) but, to our knowledge, this method has never been applied to zeolites. In particular in ref 60, Marx and Parrinello used the path integrals method in a CP study of the small carbanion CH_5^+. The simultaneous application of the two methods is critically computer resources demanding, and the simulation of atomic systems as large as a zeolite model will be delayed until the computer power will enormously grow, but the past experience could suggest that this might happen at a time not so remote in the future.

III. Simulation of Diffusive Processes

The diffusion of molecules sorbed in zeolites[61] can be described, at space and time scales much larger than dimensions and characteristic motion times of molecules, using Fick's equations.[62] Fick's equations are able to model a number of special transport phenomena occurring in zeolites but cannot describe the underlying microscopic mechanisms. In industrial plants and in most experimental settings related to the diffusion of guest molecules, zeolites are used in the form of powders, whose grains are more or less perfect crystallites, with a size usually on the order of 10^{-6} mm. Therefore, the zeolite powders do not fill all the available space, and the interstitial volume is occupied by a fluid (gas or liquid) made of the substance to be sorbed, possibly embedded in a solvent which is not adsorbed in the zeolite or in an inert gaseous carrier. Following the opinion of the experimentalists,[63] there are at least five limiting types of diffusion for the molecules flowing through the zeolitic material.

(i) Unrestricted intracrystalline diffusion: the molecule moves in the channels and cavities of a crystallite without crossing the surface of the solid or extended crystal defects.

(ii) Modified intracrystalline diffusion: the particle crosses extended (*e.g.*, dislocations, mosaic boundaries) or localized (*e.g.*, vacancies, cations in non crystallographic positions) crystal defects hindering or, sometimes, enhancing its motion.

(iii) Restricted intracrystalline diffusion: the molecule is reflected at the crystal boundary due to a very low probability of desorption.

(iv) Intercrystalline diffusion: the molecule migrates between different crystals, so it is sorbed most of the time but not confined to the same crystal. Sometimes this type of diffusion involves surface film formation and diffusion on the zeolite surface.

(v) Diffusion in the fluid phase: the particle remains in the gas or liquid phase, confined only by the walls of the vessel containing the sample.

At sufficiently low temperature or at short time scales case i must prevail, but at increasingly higher temperature and time scales all the other cases will eventually occur. Therefore, the effective large time scale diffusion coefficient is the result of a complex mechanism and will depend on the different diffusion coefficients characteristic each of the considered cases. Moreover, the value of the measured diffusion coefficient will depend on the size and time scale at which the experimental technique operates. In the recent book by Kärger and Ruthven,[61] as well as, synthetically, in a paper by Bull *et al.*,[64] the different experimental methods which are used to evaluate the

diffusion coefficients are discussed. In particular, the experimental techniques whose space and time scales are the closest to the ones accessible to MD simulations are inelastic neutron scattering (INS) and nuclear magnetic resonanace (NMR) spectroscopy (PFG, *i.e.*, pulsed field gradient NMR; linewidths, ^{2}H T_2 NMR and ^{2}H and ^{1}H T_1 NMR), and these are the most used for a comparison with MD results. Other techniques are uptake measurements and zero length column and chromatography, which show space and time scales much larger than the simulation ones and do not allow one to distinguish among the above discussed different cases of diffusion. The diffusive processes occurring in zeolites are influenced by defects and in turn they can induce structural changes (for a detailed discussion, see ref 65). In particular, besides the usual defects which are found in solids (vacancies, dislocations, *etc.*), the substitution of Si atoms with Al, which are characteristic of zeolites, entails (1) a structural disorder if the Al atoms do not fully occupy crystallographic positions, because Al−O distances are about 0.15 Å larger than Si−O distances, and (2) the presence of extraframework charge-compensating ions (usually metallic cations, but sometimes protons which are chemically bound to the surface oxygen atoms) often in crystallographically disordered positions.

Therefore, the guest molecules experience a more or less different potential depending on the nature and the spatial distribution of the ions and the structural changes in the aluminosilicate framework associated with the Al/Si substitution, and accordingly the diffusive process can be more or less modified. Moreover, in some zeolites the tilt of TO_4 tetrahedra is energetically not demanding, so that phase transitions and disorder may be induced by small (on the order of some k_BT) energy amounts. Phase transitions may be found also in the confined fluid represented by the guest species.[66,67] Depending on the temperature and on the loading (number of guest molecules per unit cell) this fluid can transform from a liquid or gas-like phase to a solid-like one, where the sorbed particles maintain evenly spaced average positions. The usual space and time scale of MD calculations (systems containing up to some thousands of particles corresponding to a few zeolitic unit cells and simulations lasting from some picoseconds up to some tens of nanoseconds) are suitable for studying the diffusion of types i, iii, v, and, with some effort, type ii. In order to estimate roughly the minimum duration of a MD simulation for the evaluation of the diffusion coefficient, it possible to proceed as follows. For most zeolite, the minimum path length that must be covered by a sorbed molecule to say that it "diffuses" and it is not subject to a localized motion is on the order of 10−14 Å, *i.e.*, the mean square displacement $\langle \Delta r^2 \rangle$ should be on the order of 100−200 Å^2 or $1-2 \times 10^{-18}$ m^2. From Einstein formula (eq 4) it follows that the minimum duration of a simulation should be

$$t_s \geq \frac{\langle \Delta r^2 \rangle}{6D} \approx (2 \times 10^{-19}\ \mathrm{m}^2) D^{-1} \qquad (12)$$

where the time is given in seconds if D is expressed in m^2 s^{-1}. Therefore, if $D = 10^{-10}$ m^2 s^{-1}, a typical value for small molecules in zeolites, t_s should be about 2 10^{-9} s, or 2 ns, which is a relatively long simulation. For molecules with smaller diffusivity and for diffusion mechanisms involving the crossing of energy barriers, like type iv, special simulations techniques that have been applied to study chemical reactions can be used (see section I.C above). It is worth noting that the time scale accessible to MD simulations is increasing rapidly as computers become faster and more powerful, so recently some calculations for the study of diffusive processes lasting only some tens of picoseconds have been reported, but actually analogous simulations often overcome 10 ns.

A. Diffusion of Spherical Particles

Since the first attempts to use MD for the simulation of diffusive processes in zeolites, sorbate molecules which could be represented by spherical particles have been preferentially chosen. This was because of the easier modeling which is required for the interactions in such systems; the saving of computer time and storage (in early times) and the possibility of performing very long simulations (in recent times); the high mobility of small molecules which entails both the need for fewer computer resources and the greater simplicity of the systems aiding the development of statistical mechanical razionalization of the diffusion mechanisms; and, finally, the availability of experimental data. This class of molecules includes noble gases (mainly Ar, Kr, and Xe and, less frequently, Ne) and small globular molecules like methane and CF_4. They are usually modeled as soft spheres, interacting between them and with the framework atoms *via* Lennard−Jones or similar potential functions. Moreover, interactions with Si or Al atoms of the framework are usually neglected, as they are considered shielded by the O atoms which cover the inner surfaces of the channels and cavities.

1. Diffusion in Silicalite

Silicalite is the all-silica analogue of the synthetic zeolite catalyst ZSM-5. It has attracted the attention of the researchers as a candidate for MD simulations mainly because of its well-known structure containing no aluminum and therefore no charge-compensating cations or protons (thus making the simulations easier), because of the importance of ZSM-5 for its applications as catalyst, and because of the wealth of experimental data on the diffusivity available. Its framework structure comprises two different channel systems, each defined by 10-membered rings. Straight channels with an elliptical cross section of approximately 5.7−5.2 Å are parallel to the crystallographic axis *b*, and sinusoidal channels with nearly circular cross section of 5.4 run along the crystallographic axis *a*. The resulting intersections are elongated cavities up to 9 Å in diameter. One crystallographic cell contains 288 atoms (96 Si, and 192 O). Silicalite shows a reversible phase transition at about 340 K and exhibits monoclinic symmetry ($P2_1/n11$ space group) below and orthorhombic symmetry (*Pnma* space group) above the transition

Table 1. Characteristic Features of MD Simulations of Methane in Silicalite[a]

ref (year)	loading (molecules per uc)	structured (ST) or spherical (SF) guest molecules	fixed (F) or vibrating (V) framework including $n \times n \times n$ uc	time step (fs)	duration (ps)	T (K)	computed quantities (comparison with expt)
71 (1989)	4, 12	SF	F $3 \times 3 \times 3$	1.5	6	300	D (good)
73 (1990)	12	SF	F, V $1 \times 1 \times 2$	1.0	200	300	D (good) ΔH (good)
76 (1990)	0, 4, 8, 12, 16	ST	F $2 \times 2 \times 2$ to $4 \times 4 \times 4$	1.0	50	200, 300, 400	D (good) ΔH (good) D_r (fair)
135 (1991)	8	ST	F $1 \times 1 \times 2$	1.0	50	298	D (good)
136 (1991)	1, 2	ST	M $1 \times 1 \times 2$	1.0	120	300, 600	D (fair)
78 (1991)	1 ÷ 8, 12, 16	ST	F $2 \times 2 \times 2$	6, 11	611 ÷ 4890	298	D (good) ΔH (good)
79 (1991)	2, 6, 12	SF	F $1 \times 1 \times 1$	20	30	200, 300, 400	D (good) ΔH (good)
83 (1992)	12	SF	F, V $1 \times 1 \times 2$	1.0	200	170, 200, 300, 450	D (good) D_{xyz} (fair) ΔH (good) E_a (good)
84 (1992)	0.5	SF	F, V $1 \times 1 \times 2$	1.0	200	300	D (fair) D_{xyz} (fair) ΔH (good)
137 (1992)	4	ST	V $1 \times 1 \times 2$	n.a.	100	150 ÷ 750	D (good) ΔH (good)
85 (1993)	0.5	SF	F, V $1 \times 1 \times 2$	1.0	200	300	D (fair) D_{xyz} (fair)
138 (1993)	0, 4, 8, 12, 16	ST	F $1 \times 1 \times 2$	1.5	60	200, 300	D (good) ΔH (good) E_a (good)
49 (1993)	0, 2, 4, 6, 8 10, 14, 16	SF	F $2 \times 16 \times 2$	5.0	200, 3000	300	D_t (n.a.)
139 (1994)	4	ST	V $1 \times 1 \times 2$	0.5	n.a.	300	D (fair) IR, Raman spectra (good)
142 (1994)	4	ST	F, V $1 \times 1 \times 2$	n.a.	41	300	D (fair) IR, Raman spectra (good)
140 (1995)	4	ST	V $1 \times 1 \times 2$	0.5	42	300	D (fair)

[a] References for experimental values are found in ref 61 and in the original papers. The comparison with experiments is evaluated as follows: good, within ±10%; and fair, same order of magnitude. Abbreviations: D, diffusion coefficient; D_{xyz}, anisotropic diffusion coefficients (when compared with experiments); D_t, transport diffusivity; D_r, rotational diffusion coefficient; ΔH, enthalpy or heat of adsorption; E_a, Arrhenius activation energy for diffusion; uc, unit cell.

temperature with cell parameters $a = 20.076$ Å, $b = 19.926$ Å, and $c = 13.401$ Å. Both structures have been recently determined by van Koningsveld *et al.*[68,69] The cell parameters are similar for the two structures, and the deviation from othogonality of axes in monoclinic structure is only 0.67°. From 1989 on, a series of MD simulations of spherical particles representing rare gas atoms or small spheroidal molecules adsorbed in silicalite were reported in the literature. In the papers discussed below silicalite was assumed to exhibit no electric field on adsorbed species. Indeed, on the basis of the results of calculations using the Ewald summation technique,[70] the electrostatic terms in the methane−silicalite potential yielded only a 1% difference in the total potential energy of the molecule. Furthemore, in the short-range interactions between guest and host the interactions with the Si were ignored because they are well-shielded by the oxygen atoms of the SiO_4 tetrahedra. Following these general features two different approaches were used to study the mobility of particles represented by soft spheres in silicalite. In the first approach the silicalite framework was kept rigid, assuming that the vibration amplitudes are sufficiently small to be neglected and that the mobility of the framework should not influence, in a system of nearly cylindrical channels, the diffusion mechanism. The alternative approach included, at least as an approximate model, the vibrations of the framework in the simulations and led to interesting results, which are discussed below. In Table 1 some characteristic features of these simulations are collected. The first report about a MD simulation of the diffusion of methane in the pores of (rigid) silicalite, by Trow and Iton,[71] appeared as a Recent Research Report Presented at the 8th International Zeolite Conference, Amsterdam, The Netherlands, in July 1989. In the first published work on this peculiar topic, Pickett *et al.*[72] simulated the diffusion of xenon, always assuming a rigid silicalite framework, just some months after the first paper on silicalite including the vibrations of the framework[73] appeared; in the last case methane was again the guest molecule. The potentials used in the calculations were almost invariably of the Lennard−Jones 12−6 form. For methane, two sets of parameters for the guest−host interactions (yielding for silicalite equivalent results) were adopted. They were derived from those pro-

posed by Ruthven and Derrah[74] and by Bezus *et al.*,[75] respectively. For the fixed framework model, in some cases[49,76] the potential energy acting on the sorbed molecule was evaluated for a tridimensional grid in the accessible volume and then interpolated using smooth continuous functions to derive the force. The simulations[49,71−73,76−89] consisted typically of an equilibration run followed by production runs of some hundreds of picosecond from which the transport properties of the system were calculated, whose duration satisfied the requirement proposed above at the beginning of section III, as D is on the order of 10^{-9} m^2 s^{-1}, except for Xe at low temperature. The simulation box consisted usually of $1 \times 1 \times 2$ unit cells ($20.1 \times 19.9 \times 27.3$ Å^3) or $2 \times 2 \times 2$ unit cells and in some cases of $3 \times 3 \times 3$ or more unit cells, with periodic boundary conditions. Different loadings, ranging from 1 to 16 particles per unit cell, were studied, and infinite dilution was simulated by eliminating the guest−guest interactions without reducing the number of particles in the box. The simulations were performed for temperatures ranging from 77 to 450 K, mostly in the NVE ensemble but, for fixed framework calculations, sometimes the NVT ensemble was adopted by employing suitable constant temperature algorithms. Usually both the computed heat of adsorption and the diffusion coefficients were close to the experimental values, often within the experimental error bounds for the fixed framework calculations as well as for the vibrating framework model. In Table 1 the characteristic features of the MD simulations of methane in silicalite are collected, as an example of the obtained results and of the evolution of the technique. We preferred not to do so sytematically for all the other simulations because the differences of the models and the enormous range of the trajectory lengths could be misleading when comparing the various results. Moreover, with a few exceptions, the most interesting experimental data, *i.e.*, the diffusion coefficients, are lacking or span over several orders of magnitude (see ref 61). As for the diffusive process mechanism, some general features were recognized in the above quoted papers. It was observed that by increasing the density of adsorbed molecules the role of channel geometry is diminuished and the dominant effect on the diffusion is the short mean free path of the molecules. This conclusion was drawn by evaluating the diffusion coefficient as a function of the number of adsorbed molecules per silicalite unit cell and by observing that at higher loading the diffusion process is hindered by an increasing number of collisions between sorbed molecules. Indeed, both experimental and computed diffusion coefficients decrease as the loading is increased. Separate diffusion coefficients for the x (sinusoidal channels), y (straight channels), and z directions were evaluated in several cases. The values for the anisotropies of D and the activation energy of diffusion which are reported show that D_y is about twice D_x and that D_z is much smaller than the others, while the activation energies for diffusion are almost equal, so the difference between the diffusion coefficients comes from the different values in the preexponential factor D_0 (eq 8) rather than from any large differences in diffusion barriers along the separate channels. This means that in the model the molecules see the framework like an energetically homogeneous medium, but due to the complex path, the diffusion along z and x is more hindered. This conclusion is valid for all spheroidal molecules diffusing in silicalite and was confirmed also by a random walk procedure by Kärger.[90] In other words, to move along x and z a molecule needs to change its direction and velocity quite often, so its diffusive motion is slower if compared with the motion along y. In some papers[72,77,80] the authors calculated the distribution of the sorbed molecules along the straight and sinusoidal channels. The resulting distributions for the two channels predict at low concentration a high probability for the sorbed molecules to be near the center of the two channels, but at higher concentrations, packing constraints force them to occupy the intersections. This is a general feature for small molecules in silicalite and had been evidenced by June *et al.*[91] by Monte Carlo simulations for methane, *n*-butane, and hexane (see also Figure 4 above for a recent simulation of ethane[50]). Following these results, it may be suggested that the dynamics of the diffusion can be described as a series of jumps from a preferred position to another one in the channels, whose fate (remaining in the same channel or deviating into another one) is determined by the specific way in which the relatively higher potential energy region of the intersections is crossed. El Amrani and Kolb[81] applied for the first time a log−log plot of $\langle \Delta r^2 \rangle$ to the study of the diffusion mechanism (see section II.B above) and in particular of the transition between Newtonian (deterministic) and Einstein (random) diffusive regime. The paper by Maginn *et al.*,[49] where NEMD was applied to study the transport diffusivity of methane in silicalite, deserves special mention. They distinguished between the self-diffusivity D (see section II.B above), which is an equilibrium property, and the transport diffusivity D_t, which is a nonequilibrium phenomenon and gives the proportionality between the sorbate flux and the concentration gradient. They should coincide only at very high dilution, but under typical conditions they are different. The authors developed a statistical mechanical method and, accordingly, they designed two different NEMD techniques to evaluate D_t. In the first technique, a concentration gradient is set up in the zeolite simulation box (suitably elongated along an axis, namely y, by including $2 \times 16 \times 2$ unit cells) and the equation of motion are integrated in the usual manner. By monitoring the relaxation of the concentration gradient and fitting it to the appropriate continuum solution of the diffusion equation (see, *e.g.*, ref 62), a transport diffusivity is obtained. This method is computationally intensive, and to overcome this difficulty, a second technique, referred to as "color field" NEMD, was adopted. In this technique the response of the system to a small constant external field (acting as a drift on the sorbate molecules which are considered as "colored") is measured and related to the transport diffusivity through the application of the linear response theory. The simulation results predict that the self-diffusivity and transport diffusivity show similar values at

infinite dilution, as expected, but diverge up to 2 orders of magnitude for the highest loading (16 molecules per unit cell), the larger being D_t, which increases with the loading, contrary to D. The analysis of ^{129}Xe NMR chemical shift in silicalite was performed by Vigné-Maeder[82] using the results of MD simulations at infinite dilution with the assumption of a rigid zeolite lattice for temperatures ranging from 100 to 450 K. This was possible because the chemical shift is usually interpreted in terms of collisions between xenon and cavity walls, and some approximations of the correlation between the chemical shift and the dynamics of xenon in the cavity were proposed. The results were good, but in our opinion, they should be verified with a vibrating lattice model, because the number and the energetics of collisions is affected by the rigid lattice assumption (see the discussion reported just below). Demontis *et al.*[73,83−87] studied the diffusion of methane in silicalite using a flexible framework approach. To model the framework, the same potential (harmonic form) as for anhydrous natrolite[20] and zeolite A[92] was adopted (see section IV.A below), while methane molecules were represented by soft spherical particles interacting with the framework and among themselves *via* suitable Lennard−Jones potentials. A loading of 12 methane molecules per unit cell[73,83,86] or infinite dilution[6,84] was simulated. Fixed framework runs were also performed to check the effects of switching off the lattice vibrations. The first effect of the vibrations of the framework is that the methane molecules form a subsystem in a canonical ensemble. In other words the methane molecules "see" the motion of the framework like a heat bath allowing energy exchange. This can be easily seen by calculating the mean square fluctuations of the temperature for the methane molecules which are in line with the theoretical values obtained following Lebowitz *et al.*[93] for a canonical ensemble. In summary, the total system (oscillating framework + methane molecules) is microcanonical (NVE) while a part of it (the methane molecules) behaves like a canonical ensemble (NVT) by exchanging energy with the framework. Besides this interesting observation, some other influences of the vibrating framework on the diffusive process of the methane molecules can be evidenced. They concern mainly computed diffusion coefficients, potential energies distributions, lifetimes of dimers and clusters, and number of collisions. At first sight the values of the diffusion coefficients for vibrating and fixed framework are similar, but by considering the velocity autocorrelation functions, relevant differences are detected. When methane molecules encounter each other or collide with the walls of the channels, backscattering occurs and results in negative velocity correlations. The effect of the rigid framework on the velocity relaxation is to cause a little shortening of the crossover time and to enhance the region of negative and positive correlation, the first and second peak in the vacf's. Since the self-diffusion coefficient is proportional to the time integral of the velocity correlation function, the diffusion coefficients are quite similar for fixed and vibrating framework simulations. An attempt to explain this fact could be made by realizing that the walls of the channels in the vibrating framework approach are softer and then less able to give an effective backscattering; on the other hand, the steric effect of lattice vibrations are responsible for the reduction of the second peak in the positive correlation region. A more evident influence appears when considering the distribution functions of the potential energy between pairs of methane molecules. For a vibrating framework the potential energy distributions are higher in the negative region, while in the positive repulsive part they decay more rapidly. In the case a of fixed framework the tails of the distributions are very long and they are not negligible even at some 10 kcal/mol. Therefore, high-energy collisions are more frequent in the fixed framework simulations. This finding could be explained considering the elastic backscattering of the sorbed molecules colliding with the fixed framework walls. Moreover, the analysis of the MD results shows that dimers and clusters of sorbed molecules are formed during the diffusive motion. Their mean lifetime has been evaluated and it was found that they are reduced by lattice vibrations. This effect is more evident for low temperatures and can be explained by the energy exchange with the framework walls. Finally, the number of binary and multiple collisions is different for fixed and vibrating framework. Lattice vibrations enhance the number of binary collisions for temperatures higher than room temperature (for a loading of 12 methane molecules per unit cell) while multiple collisions are inhibited. On the contrary, in fixed framework simulations an exaggerated number of multiple collisions take place. This finding confirms the remarks about the behavior of the potential energy distributions. In conclusion, the energy exchange due to the vibrations of the framework in silicalite gives rise to significant effects on the motion of sorbate molecules and the use of a rigid framework for simulating chemical processes, where the number and the energetics of the collisions are crucial points, could be severely misleading. From the papers reporting the simulations at high dilution,[84,85] it emerges that the influence of the vibrating framework on the diffusion mechanism of small molecules sorbed in silicalite is not as dramatic as in the case of 12 molecules per unit cell. In the absence of the collisions between sorbed particles, the diffusion is controlled by the interactions and collisions with channel walls. However, the velocity autocorrelation functions for the motion along y show, especially for the vibrating framework model, an unusual trend. They are substantially all positive with oscillations approaching zero in their minima. This behavior can be accounted for by supposing that in their motion along y methane particles maintain substantially the initial direction, slowing down or stopping after some tenths of a picosecond, restarting, and stopping again, and so on. In favor of this picture is the behavior of the potential energy surface (see refs 78, 79, and 94) showing a number of noncollinear minima along the straight channels. When the molecules come close to these minima, they are slowed down and their trajectory is deviated toward the opposite side of the channel. This kind of motion could be described also

as a series of "jumps" of different length, and it is consistent with the assumptions proposed by Jobic *et al.*[95] for the interpretation of quasi-elastic neutron scattering experiments on diffusion of methane in ZSM-5 zeolite (isomorphous with silicalite). In two recent papers[88,89] Yashonath and Bandyopadhyay investigated the diffusivity of spherical Lennard−Jones molecules (having always the same mass of 40 amu) as a function of their diameter, using both fixed and flexible framework models. An interesting result is that the diffusion coefficient shows a peak when the diameter of the adsorbate approaches the channel diameter; this peak is more evident for fixed framework simulations. This finding can be explained by considering that, when the size of the sorbate molecule fits the diameter of the channel, the radial force acting on a sorbate molecule is nearly zero, giving rise to a "floating molecule" or "levitation" or superdiffusivity effect, which was predicted by Derouane and co-workers[96−99] to be detectable in any type of confined region, irrespective of its geometry. Therefore, they showed that a naive geometrical criterion for predicting the diffusivity of a sorbate in a micropore is not correct, a result which has far-reaching implications in diverse fields such as, besides separation of mixtures by zeolites, diffusion across biomembranes in cells and host−guest chemistry.

2. Diffusion in Zeolites A and Y

The efficiency of migration of guest molecules depends on several factors: the Si/Al ratio, the nature of the extraframework cations, the presence of sorbed water molecules, the temperature, and the sorbate concentration. Moreover, the number and orientation of channels defining the internal structure of a zeolite influence diffusivities along with the dimensions and shape of the diffusing species. Zeolites A[100] and Y[101] have two topologically different channel structures: zeolite A with a simple cubic channel pattern and zeolite Y with a tetrahedral channel pattern. The pore system of A-type zeolites could be schematically represented by a cubic array of nearly spherical cavities (α-cages) interconnected through 8-membered oxygen rings (windows) with free aperture about 4.3 Å when not blocked by a cation. The void space in each α-cage (their diameter is about 11.2 Å) could be occupied by small molecules penetrated through the windows. In A-type zeolites the Si/Al ratio plays an important role in the adsorption and diffusion mechanism of guest molecules. In some of them all windows are free for diffusion, while in others windows are obstructed by an exchangeable cation. The number density of cations is determined by the number of aluminum atoms and by the charge of the cation. Therefore, their location and size will influence diffusion by chemical and steric effects. The framework of zeolite NaY consists of cuboctahedral sodalite cages or β-cages, made up of eight 6-membered and six 4-membered rings, that are linked by 6-membered rings of oxygen atoms. This leads to the formation of a three-dimensional net of large cavities (their diameter is about 11.8 Å) tetrahedrally connected by windows framed by rings of 12 oxygen atoms with free aperture of about 8 Å. Cohen de Lara *et al.*[102,103] studied the case of methane sorbed in zeolite NaA. Potential energy calculations[104] had shown that the NaIII (close to one of the 4-membered rings) cation is the attraction site of the cavity, and a neutron diffraction experiment[105] confirmed that at low temperature the molecule is located in the vicinity of this cation. In order to compare their experimental data with a model these authors performed molecular dynamics simulation with the following basic assumptions: one particle in a cavity, point formal charges on the (fixed) framework atoms (*i.e.*, +4 *e* for Si, +3 *e* for Al, −2 *e* for O) and Na^+ cations, and one force center on the molecule. They pointed out that the value of the electric field, like the external frequencies, seemed too high; this indicates that the charge distribution must be revised. A special feature of the adopted potential is the inclusion of the polarization energy. This kind of energy is usually important for neutral molecules, especially when adsorbed in the zeolite micropores, containing charges in the framework, and on the internal surfaces. The last ones generate high local electric field, and the vibrations of the framework can cause strong oscillations of these electric fields because the symmetry of the crystal is broken during the motion, and the charges that can be attributed to Si, Al, and O atoms are as large as about one-half of the formal charges (see section IV.B for a more detailed discussion of the last point). Indeed, some test calculations performed in this laboratory to evaluate the amplitude of these oscillations showed that in some selected points inside the cages of zeolite NaA accessible to the guest molecules the electric field may change by about ±20%, thus affecting the polarization energy (depending on the square of the electric field) by about ±50%. This problem is avoided when the framework is kept fixed, but in any case a correct evaluation of the electric field requires the computationally heavy Ewald sums or equivalent methods. Moreover, if more than one guest molecule is considered in the simulation, a lengthy self-consistent procedure is needed, because the polarization generates an electric dipole which in turn changes the electric field determinating the polarization itself. Therefore, in MD simulations polarization energy is avoided whenever possible, and it is approximated by adjusting the potential parameters in order to include an estimate of its average contribution. Fortunately, the system studied by Cohen de Lara *et al.*[102,103] was the simplest, as the framework was fixed and only one methane guest molecule was considered. In spite of the limitations of the applied model, the main features of the motion in the cavity were correctly represented: delocalization at high energy and progressive localization and trapping as total energy decreases. The position autocorrelation function related to the structure factor seen by neutron scattering was evaluated. Reports on the simulation of argon in zeolite NaCaA;[106,107] methane in the completely dealuminated model zeolite A, called ZK4;[31,108−114] and NaCaA[115−116] and xenon in zeolite NaY[81,89,106,107,117] are among the more recent publications. Yashonath and co-workers[89,106,107,117] performed a systematic investigation of monatomic spherical sorbates in the supercages of zeolites Y and A. Rates of intercage diffusion, rates of cage visits, and the diffusion coefficients have been calculated

as a function of the sorbate−zeolite interaction strength. They found that these properties exhibit markedly different dependences on interaction strength for the two zeolites, and they ascribed the observed behavior to be a consequence of the two principal mechanisms of intercage diffusion and the energetic barrier associated with them. The diffusion coefficient and the other properties associated with intercage diffusion are found to be directly proportional to the reciprocal of the square of the sorbate diameter when the sorbate diameter is significantly smaller than the window diameter. As the sorbate diameter increases, a peak is observed in all the transport properties investigated, including the diffusion coefficient. In other words, high diffusivities occur when the sorbate size is close to the dimensions of the narrowest part of the cage, which is the 12-membered window in zeolite Y or the 8-membered window in zeolite A. According to Yashonath, this effect should explain several anomalous results reported in the literature and suggests a breakdown of the geometrical criterion for diffusion of sorbates. Their results have shown that under certain conditions nongeometrical factors play a major role and geometrical factors become secondary in the determination of the molecular sieve property. It is worthwhile to note that these MD simulations, as remarked above for silicalite (see section III.A.1), supplement the earlier work of Derouane and coworkers[96−99] on the mobility of Lennard−Jones particles in a zeolite and the possibility of observing higher mobility in the channels of silicalite as pointed out by Demontis *et al.*,[73] and in silicalite and VPI-5, as noted by Yashonath and Bandyopadhyay.[88,89] Similar conclusions were drawn by Chitra and Yashonath[118] from a MD study of the diffusion behavior of binary mixtures of Lennard−Jones particles in rigid zeolite NaY. These kinds of studies are important because, in applications of zeolites as molecular sieves or as catalysts, the simultaneous diffusion of different guest species occurs, and it is interesting to understand the factors controlling the diffusion mechanisms in these situations. Chitra and Yashonath,[118] in particular, studied the diffusion coefficient of two Lennard−Jones different particles in NaY with a loading of two molecules per cage. One of the species (labeled 1) had the mass and the dimensions of xenon, while the diameter of the other (labeled 2), having always the same mass as the former, was varied. By plotting the ratio of the diffusing coefficients $z = d_1/d_2$ against the ratio of the corresponding sorbate diameters, one obtains a decreasing function with an anomalous peak corresponding to the superdiffusivity of the species labeled 1 when its dimensions fit the diameter of the windows connecting the cages. Vigné-Maeder[82] reported the analysis of the ^{129}Xe NMR chemical shift in zeolite NaY which was performed, like in silicalite (see section III.A.1 above), by using the results of MD simulations at infinite dilution with the assumption of a rigid zeolite lattice, for temperatures ranging from 100 to 450 K. Also in this case the results are good, but the influence of a vibrating lattice model should be checked. Fritzsche *et al.*[31,108−112] carried out a series of investigations on the behavior of methane in rigid ZK4. They began by verifying that even in a rigid framework the collisions between sorbed particles ensure a good thermalization, when at least two molecules per cage are present.[108] In a second paper,[31] they proposed the formulae (5−7) for evaluating the diffusion coefficient (see section II.B above), and they found that these formulae give coincident results for trajectories lasting at least 30−60 ps, depending on the loading. The diffusivity as a function of the loading and of the effective diameter of methane (modeled as a Lennard−Jones sphere), varying in the range of the values proposed in the previous literature, was studied in ref 109. The main result was that the diffusivity increases with the loading when the diameter of methane is large enough to experience a potential energy barrier while crossing the windows connecting adjacent cages. On the contrary, for small diameters, a potential energy minimum is present in the windows, and D decreases with increasing loading. This effect may be explained, also in view of the discussion reported in ref 65, by considering the higher number of collisions experienced by the sorbed molecules for higher loadings as helping the molecules to cross the energy barrier, when it is present in the windows, but slowing down the diffusion if it is not hindered in crossing the intercage passages. These studies were further extended[110,111] by developing an analytical simplified potential model mimicking the potential energy experienced by the methane molecules in the (fixed) cages, thus making very long calculations feasible. This model was applied to attempt a study of the fractal behavior of the trajectories. Finally, in a NEMD study like the above mentioned one for methane in silicalite by Maginn *et al.*,[49] Fritzsche *et al.*[112] evaluated the transport diffusivity D_t by means of a concentration gradient along one of the crystallographic axes. The concentration dependence of D_t was found to be satisfactorily represented by the so-called thermodynamic factor $d(\ln p)/d(\ln c)$ where p is pressure and c is concentration. For small concentration gradients the transport diffusivity turned out to be in very good agreement with previous equilibrium MD simulations. Also Demontis and Suffritti[83,113,114] performed extensive MD simulations of methane diffusion in a cubic type zeolite ZK4, but they used a model including the vibrations of the silicate framework. In order to understand the role of the lattice dynamics in assisting the diffusive motion of the sorbed molecules, they studied the same system also in the rigid framework approximation. Even more evidently than in the case of zeolite structures, where the micropores are essentially cylindrical, the framework oscillations were confirmed to be an essential factor in determining the magnitude of the intracrystalline diffusion coefficient. They proposed a phenomenological description of the diffusive process which needs to include at least four different time scales: (*i*) *quasi free motion* of the sorbed particles, for times shorter than about 0.2 ps, when the influence of the vibrations of the framework is not yet established; (*ii*) *oscillations about the preferred positions in the cage*, in the time interval between about 0.2 and 3 ps, where some differences between rigid and flexible lattice models is recogniz-

able, because of the different effect of collisions between the guest molecules and the framework; (*iii*) *intracavity diffusion*, lasting on average some tens of picoseconds (The diffusion coefficient begins to diverge for fixed and animated framework models.); (*iv*) *long-range diffusion*, which is controlled by the windows and shows dramatically different diffusion coefficients for the fixed (smaller) and flexible framework (about 1 order of magnitude larger). [The breathing of the windows is determining in enhancing long-range diffusivity (see Figures 6 and 7)].

Fritzsche *et al.*[115] performed a systematic MD study of the influence of the polarization interaction on the molecular motion of methane in zeolite NaCaA. While this effect has a remarkable action on the diffusion of unsatured hydrocarbons, for alkanes it has been assumed as negligible. Previous MD simulations[115,116] provided detailed information about the influence of this interaction, and stimulated pulsed field gradient PFG NMR studies[119] confirmed the polarization interaction to have a significant role on the diffusion. The computed results[115] at loadings higher than five guest molecules per cavity were in agreement with the available NMR data. In particular the authors concluded that further investigations including both lattice vibrations and polarization interaction are necessary to allow a full examination of all possible behaviors. In ref 65 some preliminary MD studies of partially dealuminated zeolite NaA, with animated framework, were reported. In this zeolite, the number of the charge-compensating cations decreases with the number of the aluminum atoms which are substituted by silicon atoms. The simulations were performed in order to elucidate the details of the diffusion mechanism yielding an increasing diffusion coefficient for increasing loading when the sodium ions are removed from the 8-membered ring windows connecting the α-cages. This unusual phenomenon was found experimentally in zeolite NaCaA, where the windows are open.[119,120] Moreover, percolation theory and experimental results[61] suggest that, in a cubic lattice, there is sharp cutoff in the diffusivity for a given fraction of the "closed" windows, and it would be interesting to investigate this problem with MD simulations. It was preferred to study increasingly dealuminated zeolite NaA instead of zeolite NaCa A because the presence of only one species of cations would greatly simplify the model and the discussion of the results. The calculations reported in ref 65 show that two main factors determining the value of the diffusion coefficient can be evidenced: the influence of the cations surrounding the 8-membered ring windows which, by attracting the methane molecules more strongly than the cavity walls, hinder the guest molecules from reaching the windows (even when they are open) and the collisions between sorbed molecules (more frequent and stronger for higher loadings) which help some of them to overcome the attraction of the cations and to diffuse into other cavities. Therefore, as found experimentally, the diffusivity increases with the loading, at least until the saturation of the loading capability of the channels is reached. Moreover, the results of this simulation show how much the distribution of the charge-compensating cations is able to change the diffusive behavior of the guest molecules, and they suggest that the nature of the ions, interacting more or less strongly with the guest molecules, can influence dramatically the diffusion mechanism and the value of the diffusion coefficient. In a recent paper, Li and Berry[121] studied the dynamics of xenon in NaA zeolite using the MD technique in order to reproduce the observed chemical shifts of ^{129}Xe. The simulations were performed at different temperatures and loadings, and the population of the possible adsorption sites was analyzed. Though evaluated on the basis of an approximate theory, the trend of the experimental chemical shifts was reproduced satisfactorily. Diffusion was not detected, because the windows in NaA zeolite are occluded by Na cations.

3. Diffusion in Other Zeolites

The MD simulation of the behavior of spherical particles in other zeolites was attempted by some researchers, but because of lack of both experimental data and accurate structure determinations, their number is limited. The diffusion of rare gases (Ne, Ar, and Xe) in a model dealuminated mordenite was studied by El Amrani.[77] Mordenite (ptitolite)[122] is a natural zeolite which is characterized by a unidimensional channel system with side pockets which can be entered from the main channels, consisting of 12-membered rings running along the *c* direction, with kinetic diameter of about 7 Å. The side pockets have entrances of diameter of about 2.8 Å, consisting of 8-membered rings along the *b* direction. In the MD simulations reported by El Amrani[77] (using the fixed framework approximation) the Ne atoms are sufficiently small to diffuse both in the main channels and along the *b* direction through the side pockets with unidimensional diffusion coefficients along the *c* direction about 3−5 times larger than those along the *b* direction. Like in silicalite, the diffusivity decreased for increasing loadings. For Ar atoms the diffusion along the *b* direction is forbidden, but they can be trapped in the side pockets, so with lower loadings, where the motion should be freer but the trapping easier, and with higher loadings, where the diffusion should be hindered but the trapping disfavored by the interparticle collisions, the diffusion coefficients are nearly unchanged. For Xe the behavior is more complex, owing to the strong interactions between the adsorbed atoms and the framework which favor the trapping in the side pockets and give rise to energy barriers for the diffusion. A complex behavior also was found by Vigné-Maeder[82] for the analysis of ^{129}Xe NMR chemical shift in mordenite which was performed, like in silicalite and zeolite NaY (see section III.A.1 and 3.A.2 above, respectively), by using the results of MD simulations at infinite dilution with the assumption of a rigid zeolite lattice, for temperatures ranging from 100 to 450 K. Indeed, in mordenite, the two-component NMR spectra have been interpreted by taking side pockets and main channels as different adsorption sites, and a partial blocking of the atoms in the side pockets must be invoked to explain the experimental spectra, especially at low temperatures. The author remarks that, for a more complete analysis, simulations with a vibrating framework model, allowing energy ex-

changes of the trapped atoms with sorbed xenon and zeolite, should be performed. Another zeolite which has been considered for MD diffusion studies is zeolite ρ.[123] The crystal structure of this material is cubic, and the pore system consists of two interpenetrating but unconnected body-centered-cubic lattices of approximatively spherical cages of diameter of about 12 Å (like the α-cages of zeolite A). The windows connecting the cages are formed by two 8-membered rings and can be approximated as short cylindrical tubes of length of about 4 Å and diameter of about 3.6 Å. The behavior of xenon, krypton, and argon[66] adsorbed in zeolite ρ was studied by MD simulations. The rare gas atoms were modeled as Lennard-Jones spheres, and the framework was kept rigid. The simulated temperature was 300 K for Xe, and 70 and 195 K for Ar and Kr. The simulations reproduced well the experimental values of the energy of adsorption, which are nearly independent of xenon loading. Indeed, the interaction energy of the guest molecules with the framework increasing with the loading are compensated by the increasing xenon−xenon repulsion. Preferred adsorption sites are in the center of the windows and near the inner wall of the cages. By increasing the loading, the mobility of the molecules present in the cage, which for 16 molecules per unit cell is like the one of a dense gas or liquid, is dramaticaly reduced, and for 24 molecules per unit cell (*i.e.*, nine molecules inside the cage), all the xenon atoms are well localized, assuming a solid-like structure (with a body-centered-cubic symmetry), even if the temperature is slightly higher than the bulk critical temperature of xenon. The same effect, though at higher loadings, is observed for Kr and Ar. The "condensation" begins for krypton (and for argon as well, although the ordering is not as pronounced) with 36 molecules per unit cell (15 per cage) at 70 K, and the atoms assume a distorted fcc structure. With 50 molecules per unit cell (21 per cage) the solid-like structure is more complex, but still basically cubic, and it is not destroyed if the temperature is raised up to 195 K. From the results of these simulations, it seems possible that in some cases the loadings corresponding to a solid-like structure of the sorbates can be reached experimentally, and it would be interesting to perform structural experiments to verify this possibility. Henson *et al.*[124] simulated the diffusion of xenon in ferrierite and in zeolite L. The crystallographic structure of ferrierite[125] consists of a two-dimensional system of intersecting channels. The pore system consists of 8-membered ring channels (3.4 × 4.8 Å) parallel to the *b* axis of the unit cell and 10-membered ring channels (4.3 × 5.5 Å) running along the *c* axis. The ferrierite-type zeolite crystallizes in the orthorhombic system (a = 19.15 Å, b = 14.12 Å, and c = 7.47 Å). Zeolite L[126] is one of a relatively small number of zeolites in which the internal pore volume is controlled by apertures containing 12 tetrahedra. Its structure is hexagonal, belonging to the space group $P6/mmm$, with cell dimensions of a = 18.47 Å and c = 7.47 Å. Its channel system consists of lobed parallel channels running along a. The simulated diffusivity of xenon in ferrierite, whose channel diameter fits the Xe dimensions, is again higher than in zeolite L, whose larger, 12-membered ring channels are larger than the Xe dimensions, and xenon atoms slide with some friction near the channel walls, while they "float" in the channels of ferrierite. Chitra and Yashonath[67] studied the melting of an Ar_{13} cluster adsorbed in zeolite L using both Monte Carlo and MD techniques. They found that the melting is favored for the adsorbed species with respect to the free one. Indeed, it occurs at 17 K as compared to 27 K for the free cluster. Finally, Bandyopadhyay and Yashonath[89] studied the diffusion of methane in rigid aluminophosphate VPI-5. Microporous aluminophosphates have structures similar to zeolites, but P is present instead of Si. The structure of VPI-5,[128] which belongs to the hexagonal space group $P6_3cm$ with a = 19.0 Å and c = 8.11 Å, contains 18 $AlPO_4$ formula units per unit cell with an alternating arrangement of AlO_4 and PO_4 tetrahedra. The channel system consists of straight channels parallel to the *c* axis, having an 18-membered ring pore opening with a free diameter of 13 Å. The adsorbed particles cannot diffuse from one channel to another one. As the $AlPO_4$ formula is electrically neutral, no charge-compensating ion is present in the channels. The simulations were performed as for silicalite (see section III.A.1) for Lennard−Jones sorbates of different diameter. Like in silicatite, it was found that the diffusion coefficient shows anomalous high values when the diameter of the sorbate is close to the diameter of the channels. The MD investigation by Keffer *et al.*[33] on unidirectional and single-file diffusion in $AlPO_4$-5 molecular sieve, which is an aluminophosphate with approximately cylindrical channels of diameter 7.4 Å[127] deserves special mention. The channels are parallel and not interconnetted, thus allowing diffusion in one direction only. Canonical ensemble MD simulations of methane and ethane represented by Lennard−Jones particles were conducted in rigid $AlPO_4$-5. Methane molecules are able to pass each other in the micropores, and they exhibit unidirectional but otherwise ordinary diffusion, *i.e.*, with the mean square displacement directly proportional to time. The Lennard−Jones particles representing ethane cannot pass each other easily in the channels and for short times exhibit single-file diffusion, characterized by a mean square displacement proportional to the square root of the time (see section II.D, eq 10). At longer time scale the contribution of the ordinary unidirectional diffusion was observed, due to nonzero probability of passing. The authors then performed the simulation of the behavior of a model spherical molecule slightly larger than the one representing ethane, for which the passing is energetically forbidden. In this case a purely single-file diffusion was observed. Effects of fluid density on adsorbate mobility were also addressed. In particular, for single-file diffusing molecules, the simulations reproduced accurately the prediction of the statistical mechanical theory (eq 11).

4. Mobility of the Charge-Compensating Cations

An interesting phenomenon occurring in zeolites is the mobility of the extraframework metallic cations, which permits cation exchanges modifying sorptive and chemical properties. Cation exchange is usually performed by using an aqueous solution

of the cations, as water enhances their mobility in the zeolitic pores and makes the extraction of the already present cations energetically feasible. Indeed, the cations coordinate to the oxygen atoms of the framework and to the oxygen atoms of the water molecules in a similar way. In anhydrous zeolites the mobility of the cations is greatly reduced, at least at room temperature, but could influence the diffusivity of guest molecules, so it is an interesting investigation field. MD simulations of the dynamics of extraframework ions have been attempted for both hydrated and anhydrous zeolites, the latter case formerly being easier. This topic has been studied by Shin *et al.*,[129] who simulated first the mobility of Na^+ ions in anhydrous zeolite A at different temperatures. Some jumps of the ions were claimed at 600 K in a 20 ps simulation time. These results are possibly qualitatively correct, but they were derived by assuming a rigid framework and relatively small charges for all the particles and in particular for the ions (0.625 *e* for Na^+). Moreover, an electrostatic potential with reduced range (by using a switching function) was adopted. Similar studies were performed also for Ca^{2+} and Ba^{2+} in zeolite A.[130−132] The approximations used in these works are questionable, because a rigid framework (as above reported for methane in silicalite) can cause an unphysical acceleration of the guest particles. Moreover, strong long-range interactions are neglected, so the potential barrier for the motion of the ions could be artificially reduced. Suffritti and Demontis[65] performed some simulations of the same system with vibrating framework using Ewald summations for evaluating electrostatic energy, at 300, 800, and 1300 K. While the mobility of the ions located in the 8-membered rings was high (with mean oscillation amplitude of about 0.8, 1.4, and 2 Å, respectively), no jump to another site was observed in 40 ps, though displacements as large as 3.1 Å (about one-fourth of the cage diameter) were detected at 1300 K. It is also possible that the potential barrier is too high to make the jumps observable in such a relatively short time. Lee *et al.*[133] studied the diffusion of the Na^+ ions in hydrated NaA zeolite, by an MD simulation including one α-cage with 28 water molecules and 12 ions. The framework was again held fixed, and the charge of Na^+ was even smaller (0.55 *e*, probably accounting for a partial charge tranfer to the solvent), but a correct representation of the electrostatic forces was used, including Ewald summations. In an MD simulation of 25 ps at room temperature a solvent-induced mobility of the ions located in the 8-membered rings was detected, but again, in our opinion, these results should be considered as qualitative (by recalling also the poor reproduction of the experimental data) because of the small sample, consisting of one-eighth of the crystallographic cell, and the short simulation time. In CaNaA zeolite, called also Linde 5A zeolite,[134] eight of the 12 Na^+ ions located near the surface of the α-cage are substituted by four Ca^{2+} cations. All the ions are located near the center of 6-membered rings, at different distances from the ring planes, and the 8-membered rings connecting the different cages are completely open. Therefore, this zeolite is interesting for diffusion studies, and in this view Suffritti and Demontis[65] performed a MD study of the anhydrous form. The simulation box consisted in one crystallographic cell, made of eight α-cages, containing 640 particles, including 32 Na^+ and 32 Ca^{2+} ions. In this case some interesting features of ion mobility were observed: for each kind of ion, the distribution functions of all the coordinates showed two maxima, separated by about 0.3−0.4 Å. This disorder appeared to be dynamical, as the same ion often jumped from a preferred position to the nearest one but always close to the center of the same 6-membered ring. The comparison with experimental neutron scattering structural data[134] is interesting, because in the experimental nuclear scattering density an elongated ellipsoid along a direction normal to the 6-membered ring plane was found. This result was interpreted by the experimentalists as implying that the Na^+ ions are located just inside the α-cage, whereas the Ca^{2+} ions are just outside, but a dynamical disorder like the one described by the MD simulations could explain the experimental finding as well. It was recalled above (see section II.A.2) how much the nature and the distribution of the charge-compensating cations can influence the behavior of the sorbed molecules. Therefore, it is possible that the disorder detected in the distribution of the ions in the simulated NaCa A zeolite plays a role in determining the diffusion mechanism of small molecules in this zeolite.

B. Diffusion of Structured Molecules

Molecules which are not represented as a good approximation by spherical particles show rotational and, more generally, internal degrees of freedom whose correlation with the diffusive process can be studied by MD technique. In particular, the flexibility of a molecule can improve the diffusivity, especially in zeolites with micropores of complex geometry and in principle, the vibrations of the framework could couple with rotational and other internal motions and influence the dynamical behavior of the sorbed species. In MD simulations structured molecules in some cases have been represented with all their internal degrees of freedom, but often some approximations have been used, both to simplify the potential model and to save computer time, as, for instance, high-frequency vibrational modes require very small integration time steps. The commonest of these approximations have been, besides keeping the molecules rigid, assuming fixed bond lengths or representing some submolecular groups, such as CH_3 or CH_2, as soft spheres, linked to other atoms or groups with rigid or flexible bonds (this is referred to as the "united atoms model"). Unfortunately, the diffusivity of many complex molecules, whose kinetic diameter is close or slightly larger than the micropore dimensions, is very low, so both accurate experimental data are often lacking and special techniques (see section II.C above) become necessary to perform MD simulations. Therefore, most applications concern relatively small molecules.

1. Diffusion in Silicalite

As recalled above (see section II.A.1) the diameter of the silicalite channels is about 5.2− 5.7 Å, and from

experimental and theoretical results it can be shown that molecules of dimensions larger than tetrametilbenzene cannot diffuse in this zeolite. However, the molecules whose diffusivities are accessible to usual MD simulations ($D \geq 10^{-11}$ m^2 s^{-1}) are smaller and, in practice, at room temperature only small saturated hydrocarbons (up to n-C_5H_{12}), water, and methanol can be treated. To our knowledge, no simulation has been published until now for the last two species, though good experimental data are available (see, *e.g.*, ref 61), so we shall report the results of MD studies for hydrocarbons only. Whatever the approximation used to represent the molecules (full structure or united atoms), their interactions with the framework were always represented by Lennard−Jones potential functions, in some cases[135−138] with the addition of weak electrostatic interactions. When they were flexible, a harmonic model[135−143] joined with a usual torsional model[136] or an expansion in the cosine of the dihedral angle[78,142,143] was adopted. Sometimes the bonds were represented by Morse potential functions[50] or their length was kept fixed.[78,142,143] The results are summarized as follows.

Methane. Rigid structured methane in silicalite was simulated for the first time by June *et al.*[76] at four different loadings and at three temperatures in the range 200−400 K, using the fixed framework model. The results were in line with those obtained by using the soft sphere approximation, but in addition the rotational behavior of the methane molecule could be studied. The rotational mobility of a molecule can be determined from the decorrelation in orientation of a unit vector $\mathbf{u}(t)$, that is fixed in the coordinate frame of the molecule and rotates about its center of mass. The decorrelation of $\mathbf{u}(t)$ is defined by $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$; from the last quantity, it is possible to derive the rotational diffusion coefficient D_r. The computed rotational diffusivities increase with loading (like in experiments in ref 95), reflecting the increasing rate of sorbate−sorbate collisions, which act to decorrelate the molecular orientation. However, their values are larger than the experimental data derived by Jobic *et al.*[95] from quasi-elastic neutron scattering, showing that the adopted potential functions could not be completely adequate and/or that the vibrations of the framework could affect the orientational decorrelation. The same model was used also by Nicholas *et al.*[138] and by Nowak *et al.*[135] for MD simulations at room temperature, yielding a good reproduction of diffusivity data but without studying explicitely the rotational behavior. In ref 138 the computed heat of adsorption was in good agreement with experimental values, and the time averaged distribution of the molecules in the channels confirmed the previous results,[91] indicating that the preferred regions for the adsorbed molecules are the straight and sinusoidal channels, while the channel intersections are avoided. Flexible methane molecules were simulated by Catlow and co-workers[136,137] (using a vibrating framework model) and by Dumont and Bougeard[139,140] (keeping the framework rigid). In these works the computed diffusion coefficients are larger than the experimental ones, but as the simulations were relatively short, the accordingly large statistical errors do not allow clear-cut conclusions to be drawn about the effects of the molecular flexibility. Neither it is possible from these works to derive information on the influence on the vibrations of the framework upon rotational diffusion and internal vibrations. However, in the papers by Dumont and Bougeard[139,140] it is shown that the distributions of structural parameters are slightly broader by going from a free to an adsorbed molecule, but the mean values of bonds and angles do not change significantly. The calculations reported in ref 136 were extended by performing MD runs of 100 ps at different temperatures, ranging from 150 to 750 K by Kawano *et al.*,[137] and an excellent agreement with experimental values was obtained for the diffusion coefficient. It was also found that, for the same methane−zeolite potential model, imposition of a rigid framework can increase D by 70%. This is an interesting result, because for methane represented by a soft sphere the diffusivity is almost insensitive to the vibrations of the framework, possibly because the energy transfer between the framework and the internal degrees of freedom of the molecule, namely the rotations, which can influence the diffusivity, cannot be taken into account for spherical guest molecules. A flexible methane molecule in flexible silicalite also was simulated by Smirnov.[142] The results of this work demonstrate that the framework flexibility does not significantly affect the structural parameters of methane adsorbed in silicalite.

Ethane. Rigid ethane in a rigid framework was studied by Nowak *et al.*,[135] but they were forced to perform simulations too short for a reliable evaluation of the diffusion coefficient; on the other hand, the computed adsorption heat is close to the experimental one. Flexible ethane, always in a rigid framework, was simulated by Dumont and Bougeard,[139,140] and the resulting value of the diffusion coefficient was only slightly larger than the experimental one, but it was affected by large statistical error. The behavior of the distributions of the structural parameters was very similar to that of methane (see above). A united atom model of ethane with a Morse potential function to represent the bond flexibility was adopted by Demontis *et al.*[50] for a long simulation of this molecule adsorbed in a flexible framework. Both sorption heat and diffusion coefficient were in good agreement with the experimental data, and the effect of the vibrational frequency of the molecule on the diffusion coefficient was checked by changing the strength of the bond potential function, so that the vibrational frequency was close to that of a vibrational band of the framework. The computed diffusivity of the molecule with lower vibrational frequency was slightly lower, probably as an effect of the slightly larger effective diameter entailed by the slightly larger oscillation amplitude, but no "resonance" effect was observed.

Ethene and Ethyne. Preliminary results of a simulation of completely flexible ethene adsorbed in a flexible framework were reported by Catlow *et al.*,[136] but the duration of the trajectory was too short to yield reliable estimates of the diffusivity. Flexible ethene and ethyne adsorbed in a rigid framework

were simulated by Dumont and Bougeard,[139,140] who found, as for methane and ethane, distributions of the structural parameters were slightly broader when going from a free to an adsorbed molecule, but with very close mean values, except for the computed C−C−H angle which is 173° for the adsorbed ethyne instead of 180° for the corresponding gas phase molecule.

Propane. This molecule was simulated as a rigid one adsorbed in a rigid framework by Nowak *et al.*[135] While the computed diffusion coefficient is not reliable, due to the short duration of the trajectory, the sorption heat is very close to the experimental value. Completely flexible propane always in a rigid framework was studied both Nicholas *et al.*[138] and by Dumont and Bougeard,[139,140] who obtained an excellent agreement with experiments for the diffusion coefficient and for the heat of adsorption and found, as for the other small hydrocarbons, that the zeolite has a very minor effect on the structural parameters of propane.

Butane. Three papers[78,141,143] report the results of MD simulations at room temperature of *n*-butane in fixed framework silicalite both using a united atoms and fixed bond length model. In the first one, by Goodbody *et al.*,[78] fixed bond angles were also assumed, and the performed calculations are referred to as preliminary, though the simulations appear sufficiently long. For the two papers the computed diffusion coefficients are on the same order of magnitude, the one obtained with the more flexible model of propane being larger, as expected. Also, the comparison with the experimental data is satisfactory. June *et al.*[141] also evaluated the torsional angle distribution for intermediate loading (four molecules per unit cell; the other considered loadings were one and eight molecules per unit cell, respectively) which is drastically affected by the zeolite potential field. Indeed, while in the liquid the *trans* conformer population is about 61%, for the butane molecules located in the straight channels this population is 79% and 82% for the ones in the sinusoidal channes, but it is only 56% for the molecules located in the channel intersections, whose large diameter allows the *gauche* state to be substantially populated. The Fourier analysis of the center of mass motion along *x*, *y*, and *z* axes shows two distinct peaks in the *x* and *y* directions, while only the higher frequecy peak is present for the motion along *z*. The high-frequency peak, common to all components of the motion, originates in a rattling motion normal to the pore axis. The low-frequency peak indicates that the molecules shuttle between channel intersections. Moreover, the authors evaluated the orientational decorrelation (see above in this section) of the molecular axis, represented by the end-to-end vector. It is shown that the *z* component decays in a very short time (with a relaxation time of a few picoseconds), while the relaxation time for the other components is on the order of 100 ps. The slow decay in these directions is associated with the the interchange of molecules between the straight and sinusoidal channels. The study of the isomerization reaction of butane reported in this paper will be treated in section IV.A. Hernández and Catlow[143] simulated the behavior of butane in fixed silicalite having adopted the united atoms potential model[144] of Ryckaert−Bellemans for the internal flexibility of this molecule and the same Lennard−Jones potentials as in ref 141 for representing zeolite−adsorbate interactions. They computed long trajectories (1000 ps) at various loadings and temperatures. The investigation followed the same lines as ref 141 but for more extended ranges of temperature and loading, obtaining similar results. In particular, the estimates of the diffusion coefficients and activation energy were in good agreement with experimentally measured data, and the computed dihedral angle distributions showed that even at high temperature (400 K) the fraction of *gauche* adsorbed molecules remains lower than it would be for the ideal gas, giving an idea of the strength of the confinement to which the adsorbed molecules are subject. The analysis of the oscillations of the molecules in the channels and of the self-correlations of the end-to-end vector (see above) confirmed the conlcusions of ref 141.

Hexane. June *et al.* in the same paper about the simulations of butane[141] studied with the same model the behavior of hexane at room temperature and for loadings with one and four molecules per unit cell. They evaluated the same quantities as for butane, and the results are similar. Diffusion coefficients only are slightly smaller than for butane, as expected, because the larger size of hexane is partially compensated for by its higher flexibility. The inspection of the *trans*/*gauche* conformer distributions shows that, contrary to butane, very few molecules (even less than in the liquid state) are found in the *gauche* orientation in any region of the channel sytem, as the larger dimensions of hexane do not allow an entire molecule to be accommodated in the intersection region and the energetically more favorable *trans* conformer is always preferred. The orientational decorrelation of hexane shows, as for butane, a quick decay for the *z* component and slow decays for the other components with relaxation times of some hundreds of picoseconds. Also, Hernández and Catlow[143] simulated the behavior of hexane in silicalite for a loading of four moleculaes per unit cell, using the same model as for butane, extending the trajectories up to 1000 ps and spanning the temperature range from 200 to 380 K. They obtained good estimates of the diffusion coefficients and activation energies and studied the self-correlation decay of the end-to-end vector, drawing conclusions similar to those of ref 141.

Some features are common in MD simulation results[50,78,139−141] for the above considered sorbed molecules: the preferential sites are always the straight and sinusoidal channels, and the intersections are avoided, especially for low loadings, like for spherical sorbates. Moreover, small hydrocarbons are "floating" near the axes of the channels and therefore show a relatively high mobility (see section II.A.1 above). Finally, all sorbates in silicalite show a large anisotropy of the diffusion tensor, the largest component being along the straight channels, the middle along the sinusoidal channels, and the smallest (usually 1 order of magnitude smaller than the

average of the others) along *z*. This anisotropy decreases when the loading is increased, as the collisions in more dense sorbate fluids aid the molecules also to diffuse in less favorable directions. The decrease of the diffusion coefficients for increasing loadings in silicalite is an experimental finding which is confirmed by all MD simulations.

2. Diffusion in Zeolite Y

Yashonath *et al.*[145−147] performed MD simulations to study localization and mobility of methane[145,146] and benzene[147] molecules in rigid zeolite NaY. The zeolite framework, including the cations, was treated as rigid, with the ratio Si/Al = 3, since this value enables the complete filling of the sites S_I and S_{II} by the sodium ions. The host lattice was modeled by assigning effective charges to the atoms of the zeolite. For the simulation of methane in zeolite NaY, they used a realistic methane−methane potential[148−150] which had been fitted to a variety of solid and gas properties, while the interaction between methane and the NaY host was modeled by means of a short-range Lennard−Jones potential plus the guest−host Coulomb contribution. The simulation system consisted of a single periodically replicated unit cell of NaY and 48 methane molecules, initially disposed uniformly in the eight cages. The calculated properties were then obtained from averages over 25 ps, at nominal temperatures of 50, 150, 220, and 300 K. These calculations suggest that the zeolite holding potential is such that even at 300 K the motion of methane molecules is largely confined to the cage walls. Only around 300 K is there any indication of molecules near the center of the cage. The computed bimodal energy distribution suggests two energetically distinct regions of the supercage surface: one corresponds to guest molecules at or near the most favored site, while the other arises from highly mobile molecules that are delocalized on the supercage surface. From these findings an intriguing picture of the diffusion of methane in NaY can be seen. The mass transport process, at this loading, is entirely governed by the surface interactions in spite of the large volume of the NaY supercage. The cage residence time was determined from the MD trajectories by using a distance criterion to decide whether or not a given molecule belonged to a specific cage. By lowering the temperature their values increase rapidly, and only for temperatures above around 200 K do they decrease significantly. In the MD study of benzene in zeolite NaY,[147] benzene−benzene interactions were modeled with atom−atom Buckingham potentials,[151] which have been shown to yield reasonable predictions for the properties of liquid and solid benzene.[152] As in the previous case, in the zeolite no distinction was made between the Si and Al atoms, and in the short-range interactions between guest and host, the interactions with the Si/Al were ignored because they are well-shielded by the oxygen atoms of the $(Si/Al)O_4$ tetrahedra. Electrostatic interactions between all charges were included in the potential energy calculation and Ewald sums were employed to calculate the Coulomb interactions between the guest−guest and the guest−host. In neutron diffraction[153] and spectroscopic studies[154] were found two sites where the benzene molecules can be accommodated. The first one is a site near the sodium cation at the center of the 6-membered ring (the C site), while the second one is the center of the 12-membered ring window connecting the supercages (the W site). MD calculation have been carried out using one unit cell of NaY zeolite, containing two molecules/cage (16 in total) initially placed near the C sites. The higher stability found for the C site is due partly to the strong interaction between benzene and the 6-membered ring comprising the walls of the cage, while in the W site, six of the oxygens are in the plane of the benzene, three are slightly above, and three are slightly below. Thus, in the W site, the oxygen-hydrogen interactions are roughly in the plane of the benzene, while in the C site, the interactions are perpendicular to the molecular plane. The inspection of the radial distribution functions indicates that benzene remains close to the surface of the inner walls of the cage. The power spectrum obtained from Fourier transforming the center-of-mass velocity autocorrelation function of benzene shows two peaks near 20 and 110 cm^{-1}. The authors interpreted the high-frequency peak as due to the motion of benzene perpendicular to the walls of the cage, because the potential well along the direction perpendicular to the surface is steep relative to the direction parallel to the inner walls of the cage, resulting in different frequencies along these orthogonal directions. The low-frequency peak was assigned to the motion of benzene parallel to the surface. The authors plotted the trajectories of the center-of-mass of one benzene molecule in the supercage, and it was evidence that there is a considerable motion along the surface but relatively little movement perpendicular to the surface, indicating that due to the nature of the zeolite field in the supercage, the motion of benzene is highly anisotropic. As implied by the above mentioned results, the main findings of this paper are that at room temperature benzene, like methane in NaY, moves mostly along the inner walls of the cage. Even though the cage volume is considerable, it seems that at low concentrations and up to room temperature, only the proximity of the cage surface is populated, confirming the experimental finding that there are two competing sites: the cation (C) and the window (W) sites. The behavior of benzene in siliceous faujasite (siliceous zeolite Y) was studied by Cheetham and coworkers[155] using both MD and ^2H NMR experimental techniques. The simulations, in NVT (canonical) ensemble were carried out for a unit cell and one benzene molecule. Full framework flexibility was accomodated using a force field developed by Biosym Technologies.[156] The model includes charges on Si atoms (0.5236 *e*), and O atoms (−0.2618 *e*), as well as on H (−0.153 *e*) and C (0.153 *e*) atoms of the benzene molecule, which, apparently, was assumed as rigid. Simulation runs were performed at 298, 350, 400, and 450 K and were 25 ps long. As the authors themselves remark, the short trajectories limit the precision of the simulation results. Nonetheless, a reasonable agreement between the NMR and MD results was obtained, especially at the lower temperature, but the activation energy resulting from the simulations was too high (29 kJ/mol compared

with 10 kJ/mol derived from NMR data). For NaY, including the charge-compensating cations, where the electrostatic forces reduce the diffusivity, the authors estimate that trajectories lasting about 200 ns would be required, and the same research group in a more recent study[157] preferred to use the Monte Carlo random walk method to study the diffusion of benzene. Schrimpf *et al.*[158] studied the structure, energetics and diffusion properties of *p*-xylene in zeolite NaY. They found first, by constrained reaction coordinate minimization, the preferred adsoption site, corresponding to the neutron diffraction results, and then they performed extensive MD simulations (with trajectories lasting up to 100 ns) in order to study the behavior of *p*-xylene as a function of loading and temperature, in the range between 500 and 1000 K. The distribution of the molecules over the supercages, the diffusion coefficients, and the activation energies were obtained. All of the computed quantities fell in the range of the available experimental values. It was also found that the diffusivity decreases drastically with increased sorbate loading. Finally, the simulation suggests that site-to-site migration inside a supercage may be often associated with an inversion of the orientation of the aromatic plane.

3. Diffusion in Other Zeolites

Nowak *et al.*[135] simulated the diffusion of structured rigid methane in rigid mordenite[122] (see also section II.A.3) and EU-1,[159] two zeolites which are characterized by a one-dimensional channel system with side pockets. They are different because mordenite has main channels consisting of 12-membered rings running along the *c* direction and side pockets with entrances formed by 8-membered rings along the *b* direction, while EU-1 has main channels consisting of 10-membered rings running along the *a* direction and side pockets with entrances consisting of 12-membered rings along the *c* direction. The simulations were carried out at room temperature. They were only 50 ps long, but some interesting features of the diffusion were detected. Indeed, in spite of the similar framework topology of these two zeolites, in mordenite, where side pockets have entrances smaller than the diameter of the main channels, diffusion is observed in practice along the *z* (or *c*) direction only, while in EU-1, where side pockets have entrances larger than main channels, diffusion occurs along the *x* (or *a*) direction, as expected, but diffusion along the *z* direction is observed as well. Understanding the behavior of water in zeolites is important because most natural zeolites are hydrated and because water makes possible the exchange of the charge-compensating cations, a process which is essential for the preparation of industrial catalysts. However, as mentioned above, despite the wealth of the experimental data available,[61] the diffusion of water in silicalite, to our knowledge, has not been simulated until now, but the behavior of water in other zeolites has been studied by MD. In particular, flexible water in rigid natrolite was the first zeolitic system ever simulated by MD.[21] Natrolite is a natural fibrous zeolite[3,160−162] which has channels running along the *c* direction formed by 8-membered rings. The unit cell is a parallelepiped of 18.43 × 18.71 × 6.52 Å containing 120 framework atoms (80 O, 24 Si, and 16 Al) and 16 charge-compensating Na^+ ions occupying crystallographically ordered sites in the channels. At room temperature a number of water molecules equal to the number of the cations are present in the channels in ordered positions and are linked to the cations by hydrogen bonds, which hinder diffusion. When the crystal is heated, the water molecules begin to diffuse and to evaporate from the crystal, and at 558 K the anhydrous natrolite undergoes to a reversible phase transition involving a deformation of the channels.[162] In the MD simulation of hydrated natrolite at room temperature, Demontis *et al.*[21] studied the behavior of flexible water, modeled by a modified version of the central force potential by Stillinger and Rahman.[163] The framework was represented by the oxygen atoms only (carrying a charge of −0.2 *e*) and held fixed, as were the cations (carrying full charge). It was confirmed by the simulation that the diffusion coefficient of water is negligible at room temperature. The reproduction of structural properties of water was satisfactory, except for the H−O−H angle, which was smaller than the experimental one (99° instead of 108°, *i.e.*, this angle for water in natrolite is larger than for an isolated water molecule, 104.5°). The inadequacy of the model used for water was evidenced by the poor reproduction of the vibrational spectrum, as the simulated stretching modes band is blue-shifted by about 1000 cm^{-1} (about 4400 cm^{-1} instead of about 3400 cm^{-1}). These discrepancies led to a special study of the effect of an electric field upon the structure of water and to the development of a new electric field dependent potential for water[164] designed for the study of hydrated zeolites (in connection with a potential model for the framework including charges), which is currently tested in this laboratory. Leherte *et al.*,[165−172] studied the dynamical behavior of water in ferrierite (see section III.A.3 above). These authors performed their simulations of rigid water molecules in a rigid ferrierite model with a Si/Al ratio = 8. Crystallographic data and *ab initio* MO calculations were used in order to get a more precise guess about the siting of aluminum in the framework. The negative charge resulting from Si substitutions were canceled by linking protons to oxygen atoms adjacent to aluminum atoms. The electrostatic energy was computed within the pairwise approximation between all water atoms and all zeolite atoms with charges represented by the Mulliken *ab initio* STO-3G atomic net charges determined by Fripiat *et al.*[173] The other potential energy contributions (repulsion and dispersion) were treated empirically. The water−water configurational energy was described by the MCY *ab initio* potential.[174] The simulations were performed by using increasingly improved models. They started by neglecting electrostatic interactions and periodic boundary conditions,[165] and then they were included,[166,167] thus obtaining a more realistic description of the system and correct values for the adsorption enthalpy and the diffusion coefficient at room temperature. The calculations were then extended by considering different loadings and by including a more detailed structural and dynamical analysis.[168−172] By compar-

ing the O−O, O−H, and H−H radial distribution functions of liquid MCY water computed by a Monte Carlo method[175] with the results for water in ferrierite, the authors found that the coordination number of the oxygen atom in ferrierite is larger than the expected tetrahedral structure and that molecules are localized at positions close to the channel walls of the zeolitic framework. This "solid-like" character of water in ferrierite was also confirmed by the linear velocity autocorrelation functions and by the consideration of the mean square displacements, from which it was possible to estimate a diffusion coefficient on the order of 10^{-10} cm^2 s^{-1}, the same as for the experimental findings, *i.e.*, one order of magnitude smaller than for liquid water at room temperature. The calculations show that molecules in the small pores (8-membered rings) interacting with the H^+ are characterized by a more "solid-like" behavior than the one in larger pores (10-membered rings). Moreover, the authors have shown that relative to liquid water, sorbed molecules present a restricted translational motion and a higher center of mass vibration frequency. The locations of molecules determine the positions of the frequency bands in the simulated spectra and therefore allow the characterization of experimental band shapes both for IR spectroscopy and inelastic neutron scattering experiments.

IV. Simulation of the Structure and Dynamics of the Framework

A correct MD simulation of the structure and dynamics of the framework and of the charge-compensating cations is important for a realistic representation not only of the diffusive processes, as recalled above, but also for helping structural studies, and it is essential for the simulation of chemical rections, because, as they usually are endo- or exothermic, energy exchange between reactants or products and the heat bath of the framework must be accounted for. In order to study framework structure, stability, and dynamics and the position and mobility of extraframework cations, one must have some model for the interactions between the atoms which make up the zeolite. It is a hard task to develop a potential that is both physically meaningful and suitable for simulations, especially because of the complex nature of the Si−O and Al−O bonds, which possess part ionic character (which alone is an involved matter, as discussed, *e.g.*, in ref 176) and part covalent character, which, among others, includes directionality. Moreover, a realistic description of the charge distribution should take into account the diffuse and nonuniform character of the electron density which is essential for understanding the experimental electric field.[177] In order to avoid many of these problems while developing a model able to describe the dynamical behavior of the aluminosilicatic framework, Demontis *et al.*[20,73,83,86,92] have adopted simple model potentials consisting a network of neutral atoms, the nearest neighbors being connected by harmonic or anharmonic springs. This model was adopted with satisfactory results also by Schrimpf *et al.*[178] for MD simulations of zeolite NaY. More recently, Smirnov and Bougeard[179] discussed a nearest neighbors potential model for molecular dynamics simulations of zeolites, including the dependence on bond angles but not considering charges. All of these simple models can be correctly used wherever electrostatic effects can be neglected, *i.e.*, in all-silica models of zeolites, thus containing no charge-compensating cations, in which apolar molecules are adsorbed. However, electric charges on the framework atoms are unavoidable in order to perform MD simulations with mobile cations and charged, polar or polarizable guest molecules. Therefore, a number of potential models including charges and, more generally, long-range interactions have been developed.[30,136,180−183] Unfortunately, the long-range potentials require computer resources much larger than the nearest neighbors or short-range potentials do, and the extended calculations which are necessary to evaluate some quantities like the diffusion coefficients become very expensive or difficult to perform. On the other hand, the simulation of structural and vibrational properties remain feasible, and the potential models including charges, polarization effects and many-body terms are useful all the same, despite the need for faster and more powerful computers to extend their application to more demanding calculations.

A. Models without Coulomb Interactions

In order to describe the dynamical behavior of the aluminosilicatic framework without including computationally demanding potentials, Demontis *et al.*[20,92] proposed a naive approach to solve this problem. They developed a simple phenomenological model able to reproduce the main features of the structure and vibrations of the framework, in order to generate a reasonable "heat bath" for the sorbed molecule. This model was tested for two anhydrous zeolites, namely Natrolite[20] and zeolite NaA,[92] with satisfactory results, and for the diffusion of methane in silicalite[73,83−86] and in LTA type zeolites.[65,83,113,114] In summary, it assumes that the potentials for Si, Al−O, and O−O interactions are represented by quadratic functions of the displacement from a given equilibrium bond distance. No other possible contacts are included, the initial topology of the framework bonds is retained during the MD simulation, and only first neighbors are considered as interacting atoms. The directional character of Si, Al−O bonds is ensured by the O−O potential functions which do not correspond to a chemical bond but take the place of a potential depending on an angle between bonds and make calculations simpler. The quadratic form of the potentials can be interpreted as a second-order approximation of a Taylor expansion of the atom pair potentials around the equilibrium distance, in line with the harmonic approximation used in lattice dynamics calculations for crystals.[184] While this potential is able to reproduce correctly the vibrational dynamics and equilibrium properties of the framework, it cannot be used to simulate dynamical events involving large interatomic distance variations, like melting. An example of a simulated vibrational spectrum derived from this model is reported in Figure 8 for zeolite NaCaA, along with the experimental one taken from ref 180. It appears that,

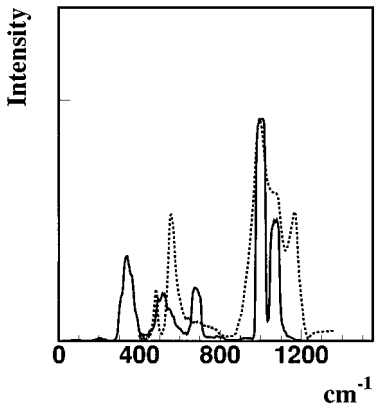


Figure 8. Simulated vibrational IR spectrum derived from the "harmonic" model proposed by Demontis *et al.*[20,92] for zeolite NaCaA at 300 K (continuous line), along with the experimental one taken from ref 180 (dashed line). Unpublished results by the authors.

although the simulated intensities are not well-reproduced, as expected (see section II.D above), the frequencies are in reasonable accord with experiment. An attempt to reproduce, by using this the harmonic potential model, the phase transition of silicalite when loaded with sorbed molecules at room temperature was also examined.[86] Silicalite undergoes a phase transition from monoclinic to orthorhombic crystal symmetry upon heating at about 340 K, but it was found by X-ray diffractometry and NMR spectroscopy that the same (reversible) phase transition can be induced at room temperature by loading the zeolite with small molecules (see ref 86 and references therein). The change of the cell parameters is small but detectable. The mechanism of the phase transition is displacive, beginning with the generation of twin domains. Sorbate-induced structural changes in silicalite were reproduced, at least qualitatively, by MD calculations using the harmonic model potential for the framework and simulating the zeolite with and without sorbed methane molecules, at intermediate loading. The behavior of the simulated system was studied by considering the distribution functions of the atomic coordinates as a structural analysis tool for the simulated crystal (see section II.A above). As recalled above, this model was adopted also by Schrimpf *et al.*[178] for MD simulations of zeolite NaY. If a more realistic description of the potential is required, terms of order higher than 2 in the Taylor expansion have to be considered. In refs 20 and 92 it was referred to as "anharmonic form". The expansion was extended to the third order for the intraframework contacts and to the fifth order for the framework−cation interactions. More recently, Smirnov and Bougeard[179,185] discussed a nearest neighbors potential model for molecular dynamics simulations of all-silica zeolites, including the dependence on bond angles but not considering charges. They showed that a consideration of the bond angle was necessary in order to better reproduce this symmetric Si−O stretching mode. Indeed, the presence of a strong O−O nonbonded term, introduced in the above mentioned harmonic model to represent the angle bending energy, leads to the fact that for symmetric Si−O stretch vibration the O−O distance undergoes variations which are larger than in the case of the asymmetric mode, and this causes a larger deviation of the energy from equilibrium values. Therefore, symmetric and asymmeric vibrational modes are affected by the potential in a different way, so the frequency gap between symmetric and asymmetric stretching modes for the harmonic model is larger than the experimental one, while for the potential model proposed by Smirnov and Bougeard the reproduction of the experimental vibrational spectra is good for siliceous sodalite (see section IV.C for a short description of the structure), silicalite, siliceous faujasite (having the same structure as zeolite X and Y, but without Al), and zeolite A.[179,185]

B. Models Including Coulomb Interactions

As remarked above, electric charges on the framework atoms and other long-range potential energy terms are unavoidable in order to perform realistic MD simulations of zeolites, in particular when mobile cations and charged, polar or polarizable guest molecules are present. In order to save computer time, some attempts to mimic their effect by using smoothly truncated potentials functions was made. Shin *et al.*,[129] for the simulation of the mobility of Na^+ cations in zeolite A, tested an approximate expression for the long-range Coulombic energy[186,187] and introduced a switching function[188,189] in order to evaluate the electrostatic potential field in the zeolite. Jhon and co-workers[190,191] studied the collapse of A-type zeolite framework with increasing temperature in the range 50−2400 K. They developed a pairwise effective interatomic potential in which a Morse-type potential function was adopted in order to represent the T−O bond in the zeolite framework. The total potentials were calculated as a sum of electrostatic, polarization, dispersion−repulsion, and Morse potential terms. The long-range Coulombic energy was treated as in ref 129. They observed, by inspection of the radial distribution functions and the distribution of T−O−T bond angles, that the framework structure became unstable by increasing the temperature and finally collapsed to an amorphous liquid-like phase at 2400 K. It would be very interesting to know if the smoothly truncated potentials functions can be generalized to other zeolites or zeolite-like frameworks. Following the procedures adopted in ref 129, Demontis *et al.*[192] attempted to study the fast ion diffusion of Na ions in nepheline,[193] a variety of tectosilicate with a parallel channel structure similar to that of zeolites. Unfortunately, they were not able to find the appropriate parameters for the switching function. On the contrary, Smirnov *et al.*[194] extended their nearest neighbors model to zeolite A containing different cations (Na and K) interacting with the framework atoms *via* smoothly truncated (using a cutoff distance of 10 Å) dispersion and Coulombic interactions (the charges were −0.55 *e* for O, 0.60 *e* for Al and Si, and 1.0 *e* for K and Na). The simulations were of reasonable length (122.4 ps) and the reproduction of experimental IR and Raman vibrational spectra was good. The same model was used by Smirnov and Bougeard[195] for a MD study of the window fluctuations in the same materials. It was shown that the extraframework cations significantly affect both the mean value of the diameter and

the amplitude of the fluctuations and that the effect of different ions is different. In particular, Na ions reduce the diameter by about 0.16 Å with respect to the corresponding one in all-silica zeolite A, which was simulated for reference, but the diameter distribution functions are nearly unchanged; K ions cause a larger contraction of the windows (0.25 Å) and induce a wider distribution function of the diameter (the full-widths at half-maximum are 0.46 and 0.96 Å, respectively). Linse and Andersen[196] have shown that potential truncation schemes are adequate for calculation of equilibrium thermodynamic and structural properties in computer simulations of liquids, but further investigations are necessary to know if these simplified versions of the long-range Coulomb interactions are efficient also in strongly inhomogeneous materials and also if they give a good representation of dynamical properties. Another intriguing problem is the value of the charges to be assigned to the atoms. Most potential models assume point charges associated with the positions of atomic nuclei, and in this view the values of charges (as discussed by Suffritti and Gamba in ref 197) can be evaluated from some accurate X-ray diffraction experiments, from the estimates of the electric fields inside the zeolitic cavities (by means of the frequency and intensity shifts of the IR spectra of sorbates[198]), from general theoretical considerations indicating for instance that the Si, Al−O bonds are approximatively half-ionic and half-covalent, or from quantum calculations on clusters reperesenting more or less large portions of zeolitic structures or even the full crystals, by using techniques such as the Mulliken population analysis. All these considerations converge toward values of atomic charges usually around one-half of the formal charges (which are +4 *e* for Si, +3 *e* for Al, −2 *e* for O) or less for the atoms of the framework, and to charges equal or slightly less the formal charges for the exchangeable cations, but these indications should include a relatively large uncertainity. It is evident that, in order to ensure the electrical neutrality of the systems, the values of the charges will depend on the Si/Al ratio, because the cations maintain approximatively the formal charge, while the other atoms bear charges smaller in proportion. The values of the charges are important also for evaluating the electric field in the cavities and channels of zeolites. This field influences, through polarization effects, adsorption heats and mobility of the guest molecules and the catalytic activity of zeolites. As mentioned above, it seems that a point charge model is not always suitable for an accurate evaluation of the electric field. Moreover, by using a point charge model, the periodical symmetry breaking due to the vibrations of the framework could cause strong, possibly unphysical, electric field variations (see section III.A.4 above). In this connection, the use of switching functions should be checked accurately. A number of potential models for zeolites including Coulomb interactions without approximations and other short- and long-range terms have been proposed for aluminosilicates, but only the ones used for MD simulations[30,136,180−183] will be discussed in the present review. For simulating the dynamics of the silicalite framework, Catlow *et al.*[136] used potential energy functions including a Coulombic term with formal charges, a short-range term consisting of an exponential repulsive function, a fifth order polynomial, a dispersion term (depending as usual on r^{-6}), and, finally, a three-body term depending on bond angles. While this model was used for extensive simulations of diffusion of methane in silicalite[137] with excellent results (see section III.B.1 above), its ability to reproduce the structure and the vibrational spectrum of silicatite was never reported, to our knowledge. Moreover, the model should be extended to materials containing aluminum and charge-compensating cations. On the basis of the results of the MD simulations using the above mentioned nearest neighbors model potentials,[20,92] Demontis *et al.*[86] have suggested some minimal requirements that a model potential for aluminosilicates should fulfill, and they developed a potential model[164] where Coulombic interactions were added to nearest neighbors potential functions, represented by Morse functions for the Si, Al−O chemical bonds, by third-order polynomials for O−O and Si, Al−Si contacts (due to the so-called Löwenstein rule, no adjacent Al centered tetrahedra are present in zeolites), and by fifth-order polynomials added to a short-range repulsive exponential term for the interactions between charge-compensating cations and O atoms of the framework. This potential is to be considered as a zeroth order approximation, strictly atom−atom, of a realistic potential for aluminosilicates, suitable to allow MD simulations of aluminosilicates containing water and other guest molecules of chemical interest; thus, it was not intended for quantitatively accurate structural studies of aluminosilicates. It was refined in order to reproduce structural and vibrational properties of anhydrous silicalite and A-type zeolites containing Na or Ca cations.[65,180] These authors have chosen to give a charge of about −*e* to the framework oxygen atoms, therefore the charges of the silicon atoms depend on the Si/Al ratio. For silicalite the charges were 2 *e* for Si and −1 *e* for O; for zeolite A, they found, by optimizing the computed structure, that the best values for the charges were 1.85 *e*, 1.27 *e*, and −1.03 *e* for Si, Al, and O, respectively. In principle, also the charge of atoms of the same species could be changed around a reasonable mean value, but they did not explore this degree of freedom. Formal charges have been attributed to the extraframework cations. The results were in reasonable agreement with experimental data, both structural and spectroscopic. Examples of the computed spectra are reported in Figures 9 and 10 for silicalite and zeolite NaA, respectively, and are compared with the experimental ones (taken from ref 180). The computed spectra show reasonable or good reproduction of the frequencies, but the comparison with the experimental intensities is not satisfactory, because of the reasons discussed in section II.D above and because of the drawbacks of the point charge model. Moreoever, this model failed to reproduce accurately the phase transition in silicalite, and some shifts in the low-frequency vibrational bands were evidenced. It was concluded that, for structures showing disordered extraframework ion distribution, point charge models

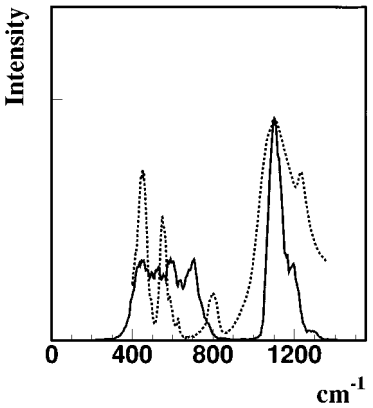


Figure 9. Simulated vibrational IR spectrum derived from the model including atomic charges proposed by Demontis *et al.*[164,180] for silicalite at 300 K (continuous line, data from ref 180), along with the experimental one taken from ref 180 (dashed line).

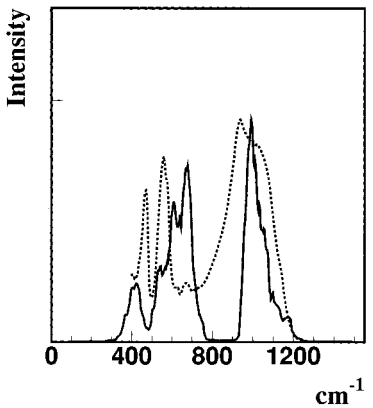


Figure 10. Simulated vibrational IR spectrum derived from the model including atomic charges proposed by Demontis *et al.*[164,180] for zeolite NaA at 300 K (continuous line, data from ref 180), along with the experimental one taken from ref 180 (dashed line).

seem to be insufficiently accurate, and polarization effects along other medium- and long-range energy terms should be taken into account. A more complex model, useful for simulations of all-silica zeolites, was proposed by Nicholas *et al.*[30] by extending the widespread molecular mechanics MM2 model[199,200] (designed essentially for organic molecules) to zeolites. Bond stretch and bond angle bend were modeled with the use of simple harmonic potentials, while Si−O−Si bond angle bend was represented by a fourth-order polynomial coupled with a harmonic Si-Si term. Dihedral angle dependent potential functions, Lennard−Jones interactions between nonbonded atoms, and Coulombic potentials were also included. Si atoms were assigned a charge of 1.1 *e*, and therefore an O charge of −0.55 *e* was used, and electrostatic interactions between 1−2 and 1−3 neighbors were neglected. The structure of all-silica sodalite (see section IV.C for a short description of the structure) and silicalite were carefully reproduced, as well as the IR spectrum of silicalite. Deem *et al.*[181] proposed a similar potential model including in principle harmonic terms for bond stretches and angles (O−Si−O and Si−O−Si), along with Lennard−Jones, Coulombic, and polarization potential functions. However, they performed MD simulations where only the harmonic terms were considered. The simulated zeolites were sodalite, silicalite, and the all-silica analogues of zeolites ρ, θ, L, and β, and the attention was focused on the dynamics of aperture dimensions at different temperatures. The evolution of the windows' dimensions was studied by direct inspection, by the histograms of their distribution, and by their Fourier transforms. The simulations revealed substantial motion of the framework atoms about their equilibrium positions. The definition, extent, and period of the fluctuations depend on the framework connectivity, but a clear and direct demonstration of the breathing motion of the zeolite pores was given. Yamahara *et al.*[165] developed another simpler model potential for silicalite, including Coulombic, Buckingham (exp-6), and Morse potential functions (the last ones for the Si−O chemical bonds). The charges assigned to Si and O atoms were 2.4 *e* and −1.2 *e*, respectively. The parameters of the model were originally determined using the MD calculations of various silica crystal structures, such as quartz, cristobalite, and stishovite,[201] but were slightly modified for application to zeolites. By performing constant pressure MD simulations, they were able to reproduce the phase transition mechanism of silicalite from the orthorhombic (high temperature) to monoclinic (low temperature) cell, though the resulting symmetry group of the simulated monoclinic phase was not the same as the experimental one. Moreover, the computed vibrational spectra were in reasonable agreement with experiment, showing that interesting results can be obtained also with relatively simple, well-tuned models. The problem involved in deriving a mechanical model for aluminosilicate frameworks are discussed in a recent paper by Hill and Sauer.[183] They demonstrate that for an accurate reproduction of the structural properties of aluminosilicates (without considering the dynamics) a complex potential force field is necessary. Moreover, in order to approximate the results of the accurate quantum calculations to which the model was fitted, they introduced atomic point charges depending on bond distances. This idea had been previously proposed by Alavi *et al.*[202] to simulate by MD the behavior of lithium ions in amorphous silica (a system closely related to aluminosilicates). They showed that this model is compatible with the usual MD simulation technique without requiring a computer effort greater than in the case of the fixed point charge model. These considerations could be one of the starting points for further developments in this field. Finally, though they were not applied to MD simulations of zeolites so far, the shell-model potentials deserve to be mentioned. They assume that atoms or ions can be represented by a nucleus bearing a positive charge and a massless (usually spherical) shell bearing a negative charge and connected with the nucleus by an isotropic "spring", so that polarization phenomena can be reproduced. These potentials, when applied to energy minimization of lattice dynamical caluculations in the field of zeolites have been shown to give good results (see, *e.g.*, ref 203), but for MD simulations they require a computer-demanding self-consistent procedure to find at each step the optimum shell positions, which has discouraged their use in this field.

C. Car–Parrinello Simulations

All the complex problems involved in reproducing the force field acting on atoms and ions of the zeolitic systems could be overcome by including in the calculations the electrons explicitely, and this is feasible by quantum mechanical methods. Unfortunately, this improvement must cope with the high number of atoms contained in zeolite crystallographic unit cells (at least 36 in the simplest, and possibly the least interesting cases, but usually in the range 252−700). Moreover, the calculations must take into account the periodicity of the crystals and the long-range Coulombic forces between nuclei and electrons. As mentioned above (see section II.D) the Car−Parrinello[14,52,53] CP method allows, in principle, MD simulations of crystals to be performed, and indeed some applications to zeolites have been recently published.[204−212] However, the number of degrees of freedom considered in this method is several times larger than for the corresponding classical system, as valence electrons are included explicitely, and, even worst, the time step must be on the order of 0.1 fs, making simulation of zeolites computationally prohibitive. This explains why, to our knowledge, the CP method was applied to three different zeolites only, both having relatively small crystallographic cells: offertite,[204,205] sodalite,[206−212] and chabazite.[211,212] Offertite[214−216] has a hexagonal unit cell, containing in the siliceous form 54 atoms (18 Si and 36 O), and shows a system of parallel channels made of small cages (cancrinite cages) connected by 6-membered rings. Other cages (gmelinite cages) showing 6- and 8-membered ring windows link the channels each other. The simulations, performed by Campana *et al.*[186−205] used the CP method as a tool for optimizing the structure by energy minimization, in order to study the effect of substituting a Si atom with an Al atom and adding correspondingly a H^+, Na^+, or a K^+ charge-compensating ion. There are only two crystallographically distinguishable positions available for substituting Al to Si atoms; six cation sites are related to the first one and four sites to the second one. Therefore, all the ten possible structures were optimized both with Na^+ and K^+ cations. It was found that the preferred site for K^+ cations lies inside the cancrinite cage, in accord with experiment, and that site selectivity is quite pronounced. On the contrary, the energetically favored positions for Na^+ cations are located in the channels, but the energy differences for other possible positions falls in a relatively small range (8−12 kJ/mol). A similar situation was found also for protonated offertite.[207] The CP-MD simulations of sodalite performed by Filippone *et al.*[206,207] required a time step of 0.1 fs and were 6000 steps long, thus lasting 0.6 ps each, without equilibration but starting from energy-minimized structures. Sodalite mineral[217−219] is obtained by condensing through 4-membered rings sodalite units in a simple cubic lattice. Each sodalite unit, or β-cage, is a cubooctaedral cavity, made up of eight 6-membered and six 4-membered rings, which are obtained by linking together six SiO_4 and six AlO_4 tetrahedra. The charge-compensating cations occupy sites located just above the center of the 6-membered rings. In natural sodalite (chlorosodalite) two Cl^- anions are located at the origin of the crystallographic coordinates and at the center of the β-cage. Filippone *et al.*[206,207] considered both the natural sodalite (containing two Cl^- anions and eight Na^+ cations) and the anhydrous sodalite (containing only six Na^+ cations) in a preliminary communication (ref 206), and they also included in a full paper (ref 207) the ideal, electron deficient sodalite structure without extra framework ions. The reproduction of structural data was good, within a few percent of the experimental values, as was the computed vibrational frequencies, which, however, could be affected by some statistical errors in view of the short duration of the simulations. Indeed, reliable frequencies can be obtained for trajectories at least 10 ps long, as is evident from the finite Fourier transform theory[29] and from the current experience in MD simulations. The CP method permits also some electronic properties to be evaluated, like the electronic destity of states, which can be compared with the experimental XPS (X-ray photoelectron spectroscopy) spectra, at least for valence electrons. This comparison was reported by Filippone *et al.*[207] for sodalite and the agreement was reasonable. Blöchl and coworkers[208−210] applied the CP method to study the behavior of water and methanol in a low-aluminum protonated sodalite, in connection with the proton transfer from the acidic site of the zeolite to the guest molecules. Indeed, this chemical step is crucial to unravel many industrially important catalytic mechanisms. In the first two papers,[208,209] the authors performed CP−MD simulations of methanol at low coverage (one molecule per acid site). It was found that the methanol molecule remained unprotonated and formed one strong hydrogen bond with the acid-site proton and one weak hydrogen bond with a framework oxygen. The calculated vibrational spectra were in agreement with the experimental ones. The same results also were obtained by Shah *et al.*[211,212] using a slightly different implementation of the CP method. In the last paper by Blöchl and coworkers,[210] the simulations were extended to water (one and two molecules per acid site, at room temperature for 2.5 ps) and to methanol at high coverage (two molecules per acid site at about 500 K for 3 ps). At low coverage water behaves like methanol, forming one strong hydrogen bond with the acid-site proton and one weak hydrogen bond with a framework oxygen (a second nearest neighbor oxygen with respect to the acid-site proton is energetically favorite); while, when two water molecules are adsorbed per acid site, the zeolite proton is removed from the framework and is shared by the two water molecules. The resulting $(H_5O_2)^+$ cluster forms one strong and one weak hydrogen bond to other framework oxygen atoms. The derived vibrational spectra were consistent with infrared data and the adsorption energies were in good agreement with experiment. These results are confirmed with "static" but sophisticated quantum mechanical calculations performed by Krossner and Sauer,[220] who, however, found that also the structure without proton tranfer is stable but less than the ion-pair structure. In the simulation with two methanol molecules per acid site, it was observed that the proton was first transferred to the nearest

methanol molecule and was then shared between the two molecules forming stronger bonds with either one or the other methanol molecule, and for a short period of time it was even found that the proton returned to the acid site. However, in general, the results of simulation of dynamical processes involving protons using *classical* MD (in the CP method, as mentioned above, only the potential energy stems from quantum mechanical grounds) are to be considered with some caution, because quantum dynamical phenomena, like energy barrier tunneling, cannot be neglected. The chabazite structure[213] has only 36 atoms in the unit cell, and it is interesting because it is an active catalyst for the condensation of methanol to dimethyl ether, the first step of the famous methanol to gasoline process, usually employing in industrial plants the more complex H-ZSM-5 zeolite having 288 atoms per unit cell. Chabazite exhibits a three-dimensional channel system with 8-membered ring windows and the Si/Al ratio is usually 3. Therefore, in real chabazite having twelve Si, Al sites, there are three protons per unit cell as acidic sites. In their CP−MD investigation, Shah *et al.*[211,212] restricted the study to a form with only one Al (And acidic site) per unit cell, in order to reduce the number of permutations to be considered, simulating a high-silica form, chabazite SSZ-13, which, in fact, has recently been prepared. Once the framework in the four possible crystallographically different configurations for the acidic sites was relaxed using the CP method, the structure, the electron distribution, and the energetics of chabazite embedding an adsorbed methanol molecule was investigated starting from a number different reasonable ways in which methanol may bind to a zeolite catalyst. The most energetically favorable situations were found, as expected, when one or two hydrogen bonds are formed with the acidic site and the zeolitic proton is tranferred to methanol, thus forming a methoxonium cation. The computed vibrational frequencies are consistent with the experimental IR spectra. It interesting to remark that these conclusion are the opposite of the results of sophisticated static quantum mechanical calculations[221] for clusters representing a portion of the zeolite surface with the adsorbed methanol molecule, indicating that the adsorbed methoxonium ion is unstable and may be represented as a transition state for the migration of the zeolitic proton from an acidic site to another one. These pioneering applications of CP method will stimulate further investigations on zeolites, which will become more and more feasible as computers become faster and more powerful.

V. Special Topics

Some recent MD simulations on zeolites have extended the application of this method to interesting investigation fields different from the usual diffusive processes and the vibrations (and structure) of the framework. As they require special techniques, these applications are still represented by a small number of examples, but they are reviewed separately because they probably represent the seeds of new important developments. In particular, the intramolecular dynamics of sorbates, the chemical reactions, and the activated processes will be treated.

A. Intramolecular Dynamics of Sorbates

The changes of the intramolecular dynamics of sorbed molecules with respect to the gas or liquid phase is an interesting field of investigation which has been explored by experimental and theoretical works, especially in connection with the vibrational spectroscopy. Indeed, frequency shifts of the vibrational frequencies of simple probe molecules like H_2, N_2, O_2,[222] CH_4,[223] and CO[224−226] give information about the electric field or the bond capacity of the various adsorbing sites, and therefore, they allow some insight in the chemical properties of zeolites. The measured frequency shifts stem from the changes of intramolecular potential energy induced by the interactions with the zeolitic framework and should be studied on quantum mechanical grounds. Indeed, this route was followed recently by Cohen del Lara and co-workers[227−229] for diatomic sorbates, but these methods are difficult to apply to polyatomic molecules, and the usual MD may be used, at least as a first approximation, to study the intramolecular dynamics of sorbate molecules. The first attempt along this line was made in one of the first MD studies of zeolites, on water in natrolite, by Demontis *et al.*[16] As reported above in section III.3, it was found that intramolecular potentials able to reproduce reasonably the internal frequencies of water molecule in the gas phase did not yield correct results for water in natrolite, as the computed frequency shift for stretching modes was completely different from the experimental one (about $+700$ cm^{-1} instead of about -300 cm^{-1}). In order to overcome this problem, an electric field dependent intramolecular potential for water was developed,[164] and applications to zeolites are in progress in this laboartory. Recently, Dumont and Bougeard[139,230] performed MD simulations of a series of flexible hydrocarbons (methane, ethane, propane, ethene, and ethyne) in rigid zeolite A[139] and silicalite.[139,230] A good agreement of computed vibrational frequencies with the experimental ones was obtained for silicalite, while discrepancies due to the cations appear in zeolite A.[139] Finally, Demontis *et al.*,[50] with a series of simulations of a flexible united atoms model of ethane in flexible silicalite, showed that resonance phenomena between the vibrations of the framework and the intramolecular ones of sorbate molecules can occur. This kind of investigation, in our opinion, should be extended and developed, especially in connection with the study of excess energy dissipation in chemical reactions occurring in the micropores of zeolites.[231]

B. Chemical Reactions

In the catalytic action of zeolites, at least *five* different aspects can be distinguished. Those most frequently mentioned are the selectivity of the reactants, the selectivity of products, and the very chemical effect of acid−base and/or transition metal catalysis. However, there are at least two other properties of zeolites which can influence the reactivity of the sorbed species: the heat bath effect of the

framework, which can dissipate the excess energy of a chemical process or furnish thermal energy to reactants or products, and the influence of the (often locally strong) electric fields present in the micropores on the electronic energy states of the sorbates. In order to apply MD simulations to the study of chemical reactions all these aspects should be accounted for. The selectivity of reactants and products is essentially a steric effect, and it was thoroughly shown above, in connection with the study of diffusion, that MD is a valuable tool for simulating this kind of effect. The heat bath effect is well-reproduced by MD, and its importance and effectiveness was demonstrated by the computer simulations. The two remaining effects are strictly quantum mechanical in nature. However, the catalytic action could be simulated (with some approximations) by MD if a good smooth fit of a reliable potential energy hypersurface of the reactive process is available. The evaluation of these hypersurfaces must be performed by quantum mechanical methods. The problems connected with the quantum calculations in the field of zeolites are thoroughly discussed by Sauer *et al.*[233] in a recent review. In summary, reliable results can be obtained only from lengthy and sophisticated methods. Therefore, in many cases the evaluation of potential energy hypersurfaces for complex reactive mechanisms could be computationally awkward, but this would not be the case for simple radicalic reactions. In any case, reasonable model potentials could be sufficient for meaningful simulations. If the hypersurface shows potential energy barriers higher than the available thermal energy, special but well-known techniques are needed to apply MD (see section II.C above). The last remaining effect, *i.e.*, the influence of the electric field, if it is not included in the potential energy hypersurface, can be accounted for directly in the simulations by using the CP method. By neglecting the last effect, which that in some cases could be of little importance, it appears that MD could be currently used to simulate chemical reactions in zeolites, but to our knowledge, only one or two attempts to perform this kind of simulation, have been made. It seems that some research groups have been discouraged, by the apparent complexity of the puzzle, to try to put together all the pieces, in spite of their computational attainability. To our knowlege, the first (and the only published as yet) example of the study of a chemical reaction in zeolites was performed by June *et al.*[141] The reaction was simply the isomerization between conformers of butane and hexane in rigid silicalite, but the adopted procedure is similar to the one that should be followed in any other case, as complex as it may be. The process of conformational isomerization is intimately linked to the interchange of sorbate molecules between the straight and sinusoidal channel systems. This is evident especially for hexane, whose length is greater than a channel intersection, so that the movement between the straight and sinusoidal channels requires that the molecule undergo conformational isomerization. Therefore, the rate of interchange between the two channel systems should not be greater than the rate of conformational isomerization. In order to quantify the rate of conformational isomerization, one must determine both the reaction order and the rate constant, k, of the reaction. In previous MD investigations[234,235] of conformational isomerization in the liquid state, which had been performed for *n*-butane, the process was assumed to have first-order reaction kinetics. To verify these assumptions, the rate of conformational isomerization of butane and hexane was monitored by two methods. The first obtains a transition-state theory (TST)[34] estimate of the rate constant, k^{TST}, by counting directly the the number of *trans/gauche* potential energy barrier crossing events in a given period of time, but gives no other information on the dynamics of the isomerization process. Moreover, this method overestimates the true rate of conformational isomerization, because of barrier recrossing, but a correction for this error can be made through a more detailed analysis of the process from long MD simulations. The second method permits the dynamics of the isomerization process to be followed by computing a normalized relaxation function (see refs 141 and 235 for the formalism) and by examining the behavior of the function. Indeed, if the process is assumed to have first-order reaction kinetics, the long time behavior of the normalized relaxation function should be described by a simple exponential decay with a time constant equal to the inverse of the true rate constant for the isomerization process, k^{-1}. Any deviation from a long time exponential decay indicates that the conformational isomerization process is more complicated than the assumed first-order reaction kinetics. To determine a statistically significant estimate of the true rate constant, a 2-ns simulation of butane in silicalite at 300 K was carried out at a loading with four molecules per unit cell. The normalized relaxation function was computed and plotted on a logarithmic axis as a function of time up to 200 ps. It was found that its decay deviated significantly for the expected first-order behavior over these time scales. Therefore, the process of conformational isomerization in the model zeolite is fundamentally different from that in the liquid, where previous investigations had confirmed first-order kinetics to be established beyond times of a few picoseconds. The authors conclude that "In alkane−silicalite system, the process of conformational isomerization is apparently governed by multiple time constants. This behavior is most probably caused by a coupling between the torsional dynamics and the position of the sorbate molecule within the potential energy field of the zeolite. As molecules move between the channel segments, they experience a significant variation in local environment. [...] Thus, the molecules are likely to possess a different rate constant for conformational isomerization within each of these regions [channel segments or intersections]". Unfortunately, the framework of silicalite was kept fixed, so the influence of the lattice vibrations on the process of conformational isomerization was neclected, but the basic conclusions should not change significantly, because these conclusions depend essentially on the structure of silicalite. Very recently, Delogu *et al.*[231,232] attempted a MD qualitative study of recombination reactions of I_2 in silicalite and in liquid CCl_4. The reaction in liquid phase was

simulated in order to get a comparison both with experimental data[236,237] and with previous statistical mechanical[238,239] and MD investigations.[240,241] A simplified model has been developed to study the reactive process. The potential acting between I atoms is represented by Morse potential functions. Two iodine atoms are embedded in a Lennard−Jones liquid simulating CCl_4 or in a vibrating silicalite lattice, and a MD simulation is started. After equilibration and 10 ps of free diffusion, a photodissociation is simulated by giving the iodine atoms a suitable velocity, and the evolution of the system is then studied for 60 ps. The observed fate of the two I atoms is a primary recombination (the direct formation of a stable I_2 molecule through a quick relaxation of the excess energy), a dissociation, or a more complex behavior, where the molecule is not stable and undergoes dissociation and eventually a recombination of the dissociated molecule occurs. The direct reaction is favored in the liquid, where the excess energy transfer, occurring via a translational−translational coupling, is more efficient, while in silicalite the reaction is usually complex, showing multiple dissociation−recombination cycles, possibly because the dissociated atoms lose energy slowly while diffusing in the channels, but after the molecule is formed, the excess energy dissipation is faster, as it occurs by vibrational−vibrational coupling. Moreover, as for the conformational isomerization of alkanes, the behavior of the iodine atoms depends strongly on the region of the channel system (sinusoidal or straight channels or intersections) where the collision occurs. These interesting results are examples of what can be obtained from MD investigations of the chemical reactions in zeolites.

C. Activated Diffusion

As remarked above, usual MD simulations are not suitable for studying the diffusive processes when a potential energy barrier for diffusion is present. In these cases special techniques must be applied. The problem is discussed by June *et al.*[242] in a paper on the diffusion of xenon and SF_6 in silicalite. These authors evaluated the self-diffusion coefficient of infinitely dilute sorbate molecules by transition-state theory (TST).[34] Then the resulting rate constants for jumping between different sites within the lattice were dynamically correct following the theory proposed by Voter and Doll.[243] These results were compared with those of Monte Carlo and MD simulations. For MD, it was shown that the equilibrium distribution of xenon in the different transition states was incorrectly reproduced at 150 K, while it became consistent with the results of the other two methods at 300 K. This finding is obviously connected with the presence of a potential energy barrier to diffusion, and at the lower temperature the kinetic energy is not sufficient to ensure a statistically significant number of crossings. In two more recent studies by Mosell *et al.*[244,245] the diffusion of Xe in zeolite NaY at low temperatures (in the range between 77 and 210 K) was investigated by MD simulation of individual trajectories started at the cage-to-cage boundary, *i.e.*, at a transition state. This procedure is exactly the same that should be used for the MD study of chemical reactions (see section II.C above). Lattice flexibility was taken into account in the simulations, and therefore, for obtaining a correct starting point a 'constrained reaction coordinate dynamics'[48] was performed. In this technique the diffusing particle is constrained to stay on the "reaction coordinate" for cage-to-cage crossing, in particular in the energy maxima along this coordinate, which are not simple to find otherwise, because the flexibility of the framework make the geometrical criteria useless. The transmission coefficients, whose product with the TST kinetic constants for the crossing gives a correct estimate of the overall kinetic constants (see, *e.g.*, ref 34), were obtained from the normalized reactive-flux correlation functions,[141,235] which were evaluated from the MD simulations.[244] The observed recrossing of the cage-to-cage boundary by xenon atoms at very low temperatures were attributed to instantaneous shifts of the maximum of the potential energy along the diffusion path due to the vibrations of the framework. At higher temperatures the simulations showed increasingly many recrossings due to the slow energy transfer from guest atoms to the zeolite lattice. These results were compared with another approximation[245], *i.e.*, modeling the diffusion as a sequence of jump events that may consist of several barrier passages. The number of jump events was calculated from the TST using the potential of mean force as a basis. In the range from 140 to 210 K, the diffusion coefficients obtained from the hopping model were found to be in excellent agreement with corresponding data from conventional MD simulations, but for lower temperatures the conventional MD did not give correct results, and the special technique using trajectories starting from the top of the potential energy barrier had to be applied. The same research group extended the study to the dynamics of long *n*-alkanes (up to C_{20}) in silicalite,[246], but using a simulation strategy which utilizes concepts from Brownian motion theory and TST theory, and compares well with the results of MD simulations of *n*-butane and *n*-hexane.[141] The above reported examples show that this special technique can be currently used to evaluate diffusion coefficients and to study diffusion mechanisms whenever high-energy barriers cause slow but measurable diffusivities, which, on the other hand, are often of practical interest.

VI. Conclusions

All the above reported results may be summarized as a series of goals that the MD computer simulation technique has achieved during the last 10 years in the field of zeolites. Many investigations have been devoted to study the diffusive processes of sorbates in a number of zeolites, but mostly in silicalite, in zeolite A, and in zeolite Y. These zeolites have been chosen because many experimental data were available, and they show diffusivities which can be reproduced using conventional MD simulations. Silicalite has the further advantage that no charge-compensating cation is present in its structure. The overall agreement of computed diffusion coefficients with experiments is good, and their values are almost always (especially for NMR and INS measurements)

within the range of experimental data, which, on the other hand, sometimes span over several orders of magnitude. Also the dependence of the diffusivities on the loading and temperature has been well reproduced. Moreover, MD simulations have confirmed previous results about the distribution of the preferred positions of the sorbate molecules in the micropores (for instance, the unexpected low occupancy of the channel intersections in silicalite) and the theory proposed by Derouane and co-workers[96−99] predicting an enhancement of the diffusivity when the sorbate molecules fit the dimensions of the micropores. On the contrary, MD simulations have helped in pointing out or establishing for the first time some interesting phenomena, such as the sliding motion of the diffusing molecules on the surface of the micropores, at least for low loadings, the size and the effects of the breathing motion of the windows connecting adjacent cages, which can become crucial for controlling the diffusion of some sorbates, and the heat bath effect of the framework for the sorbate molecules, which entails some ability of furnishing or dissipating excess internal energy in collision dependent effects (like the chemical shift) and in reactive chemical processes. It was shown also that the last phenomenon can be enhanced by resonances between the internal motions of the guest molecules and the vibrations of the framework, and resonances could be important in influencing the diffusive processes when complex guest molecules are involved. Therefore, in our opinion, the framework could be kept rigid only when the guest molecules are smaller than the critical dimensions of the micropores, they are well represented by soft spheres, they are present with high dilution, and the collisions with the framework atoms are not important for the required results, *e.g.* when only the diffusion coefficient and the adsorption heat are to be evaluated. The reproduction of the structural properties of the framework has usually been good, though the potential models proposed so far did not always reach a fine-tuning in the simulation of the vibrational spectra and of phase transitions. New perspectives and developments can be suggested on the basis of some pioneering results. In particular, the study of the diffusive processed could be extended to mixtures of sorbates, in order to cast some light onto the dynamics of reactants and products in chemical reactions occurring in zeolites. More detailed studies could include complex and flexible sorbates, using the appropriate techniques when the potential energy barriers become hardly accessible to molecules in thermal equilibrium. As remarked above, the simulation of chemical reactions in zeolites, a very interesting field because of the nearly complete lack of theoretically sound mechanism studies in spite of their intensive industrial applications, should be greatly extended. Model calculations could yield qualitative information about the general aspects of reactive processes in zeolites, while simulations using good fits of accurate quantum mechanical reactive potential energy hypersurfaces, which are now within the reach of the specialists of the field, could help in understanding some details of the reaction mechanisms. Another approach to this problem could come from the Car−Parrinello calculations which, besides furnishing parameter-free simulations of structural, electronic, and vibrational properties of the framework, could be useful for the direct investigation of chemical processes, though possibly only when fast and easy parallel computing will become of common use.

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VIII. Abbreviations

CP	Car−Parrinello molecular dynamics simulation method
INS	inelastic neutron scattering
IR	infrared spectroscopy
MD	molecular dynamics
MO	molecular orbitals
NEMD	nonequilibrium molecular dynamics
NMR	nuclear magnetic resonance spectroscopy
NPT	(constant) number of particles, pressure, and temperature (isobaric−isothermal ensemble)
NVE	(constant) number of particles, volume, and total energy (microcanonical ensemble)
NVT	(constant) number of particles, volume, and temperature (canonical ensemble)
PFG NMR	pulsed field gradient nuclear magnetic resonance spectroscopy
STO-3G	Pople minimal basis set for molecular orbitals quantum calculations
TST	transition state theory

IX. Glossary of Symbols

$\langle A^2 \rangle$	mean square amplitude of an oscillator
$C_{fg}(t)$	correlation function for the two functions $f(t)$ and $g(t)$
d_o	cut-off distance for recognizing a dimer of sorbate molecules
d_i	diameter of ith guest particle
D	diffusion coefficient
D_{id}	diffusion coefficient along an axis at infinite dilution
D_o	pre-exponential factor in temperature dependent diffusion coefficients
D_r	rotational diffusion coefficient
D_t	transport diffusion coefficient
D_x	diffusion coefficient along the x axis
E_a	Arrhenius activation energy
E_o	zero-point energy of an oscillator
F	mobility factor of single-file diffusion
h	Planck's constant
k	rate constant of a chemical reaction
k_e	elastic constant of a harmonic oscillator
k_B	Boltzmann's constant
l	average distance between molecules in single-file diffusion
N	number of particles
P	pressure
R	gas constant
t	time
T	temperature
V	volume
W	virial of a system of particles
$\langle \Delta r^2 \rangle$	mean square displacement of a particle

$\langle \Delta x^2 \rangle$	mean square displacement of a particle along the x axis
ζ	ratio of the diameter of two guest particles
ν	frequency of an oscillator
$\sigma^2(T)$	mean square fluctuation of temperature
ρ	the one-dimensional density of particles, in single-file diffusion
σ	length of a molecule along an axis, in single-file diffusion

X. References

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