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Gas sorption isotherms in swelling glassy polymers—Detailed atomistic simulations

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ABSTRACT

Detailed atomistic simulations were carried out for swelling polymer/gas systems related to experimental sorption and dilation data for CO_2 and CH_4 in three glassy polymers (polysulfone PSU, the polyimide 6FDA-TrMPD, and a polymer of intrinsic microporosity PIM-1) at 308 K (35 °C) and pressures up to 50 bar. Corresponding experiments were performed with a gravimetric sorption balance and a dilatometer based on a capacitance distance sensor. For each polymer/gas system molecular packing models were prepared and equilibrated for two reference states: the pure polymer is taken as reference for the respective "unswollen" state and similarly the state of the highest penetrant pressure reached in the corresponding experiment is taken to represent the "swollen" state. Models for the latter were constructed in agreement with experimental data (pressure, temperature, gas concentration and volume dilation). Concentration–pressure isotherms of each polymer/gas system were obtained using Grand Canonical Monte Carlo (GCMC) simulations for both reference states (depleted of gas molecules), which are in good agreement with the experimental data in the respective pressure range. As expected these isotherms – due to the simulation technique used, merely based on hole-filling in a static host matrix – do not represent the sorption behavior over a broader range of gas pressures which may involve significant structural rearrangements as well as swelling and relaxational phenomena. Nevertheless, a linear combination of the two GCMC-isotherms allows the interpolation in order to describe the nonlinear gas sorption in the glassy polymers under investigation covering the penetrant pressure range between the reference states in good agreement with the experimental results.

1. Introduction

The behavior of amorphous polymers in contact with gas atmospheres is still an area of both, fundamental scientific interest and applied industrial research. Applications of gas/polymer systems range from the use as barrier materials or protective coatings to active layers in sensor applications ('artificial nose') and of course the field of gas separation membranes. In many of these applications, higher concentrations of small penetrant molecules may lead to changes of the polymer, such as swelling or plasticization [1,2]. This effect is utilized in processing applications, where, e.g., supercritical carbon dioxide (CO_2) can be used as a plasticizer [3].

The phenomenon of penetrant induced plasticization of glassy polymers is also observed in gas separation membranes [4]. The observed plasticization and the associated relaxations in the polymer matrix change its local structure and *free volume*, and thereby affect the permselectivity of the material [1,2,5]. The origin and mechanism of these structural relaxations are not fully understood, yet, as are the factors that influence solubility and mobility of the plasticizing penetrant. At present, this lack of knowledge still leads to development strategies for new or optimized materials, which are in part determined by trial and error. A deeper understanding of the phenomena that accompany gas sorption on the molecular level is therefore needed to control material properties and enable a targeted design of functional materials. In order to address this topic, in this work laboratory experiments are combined with detailed atomistic molecular simulations. In a previous publication we presented our approach, including also a thorough kinetic analysis of the sorption and dilation experiments as well as their interpretation in the framework of phenomenological models, using the example of carbon dioxide in polysulfone (PSU) [6]. Molecular models of selected reference states (with respect to penetrant loading and dilation)

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were analyzed in regard to their free volume characteristics and sorption isotherms were calculated based on Grand Canonical Monte Carlo (GCMC) simulations. In this paper we focus on the sorption isotherms obtained based on this approach for additional glassy polymers and carbon dioxide and methane.

1.1. Molecular modeling of glassy polymers

Forcefield based molecular dynamics (MD) simulations are performed in femtosecond steps, but reliable results are usually not obtained until a nanosecond of net simulation time has been attained. Using periodic boundary conditions it is feasible to represent the essential behavior and properties using relatively small models of a few thousand atoms [7]. Molecular packing models of amorphous polymers may be analyzed using several established methods in order to reveal structural features on an atomistic level, such as densities and the free volume distribution [8], or dynamic properties, such as kinetic energies or diffusivities of penetrant molecules [9,10]. from a molecular dynamics (MD) simulation run.

Limitations with respect to size of the models as well as of the simulation timescale up to several nanoseconds still constitute a significant constraint when glassy polymers exhibiting a complex structure and higher fractional free volume (FFV) are to be investigated. However, just these features often have to be regarded as a prerequisite for materials with potential as high performance materials with good permselectivities for membrane separation applications. This is even more true when dilation and plasticization phenomena affect the penetrant sorption and transport in the polymeric matrix which is often the case at higher concentration levels of penetrants strongly interacting with the polymer.

Initiated by membrane applications, several investigations took place in the field of gas sorption in glassy polymers that utilize detailed atomistic molecular simulation techniques. The basic simulation techniques related to materials science of polymeric membranes are well documented in [11].

For the calculation of solubilities of small penetrants in dilute solutions, the Widom method [12] has been implemented for glassy polymers by Gusev and Suter [13,14]. A more generalized direct-particle-deletion scheme for the investigation of larger penetrants at higher concentrations has been developed by Siegert et al. [15] as well as by Spyriouni et al. [16] on the basis of an algorithm applicable to model systems by Boulougouris et al. [17]. Cozmuta et al. [18] investigated solubilities of several polymer/gas systems using a combined MD and GCMC simulation method to calculate the Henry's constant (see Eq. (4)). Wang et al. [19] recently presented a study of diffusion and solubility in the high free volume polymer PTMSP, linking the temperature dependency of the permeability to that of the distribution of cavity sizes, with reasonable agreement to experiments. Also Eslami and Müller-Plathe [20] describe a novel computational method [21] to calculate solubilities of several gases in polystyrene over a wide range of temperatures and pressures. With a combination of calculated excess chemical potentials and partial molar volumes, both by utilizing the Widom test particle insertion method, they predicted sorption isotherms for several gases in polystyrene which are in good agreement to experimental data.

As mentioned above, some methods already exist to predict gas transport properties of polymers from simulations [22]. Often well agreeing results were obtained for ideal circumstances – small penetrant gases, rubbery polymers and low penetrant concentrations; they frequently failed when applied to less moderate conditions – e.g., high penetrant concentrations, long time scales, large penetrants or glassy polymers with complex structure [7,11,23].

The time scale of MD simulations is limited to a few nanoseconds and therefore it is not possible to directly simulate relaxations of the glassy matrix as they are observed experimentally. Experiments, on the other hand, yield results of the real macroscopic system, and though molecular details cannot be observed individually, the accumulated effects permit the analysis through models on a statistical or phenomenological basis.

The aforementioned gas induced plasticization of polymers presents such a case where the gap of time scales between experiment and available simulation time amounts to several orders of magnitude.

As in previous work [6,24–26], we pursue a new approach of a combined analysis of experimental and modeling results in order to establish, where possible, a convergence of boundary conditions or, alternatively, identify and isolate comparable aspects of these seemingly incompatible methods. This work concentrates on the investigation of sorption isotherms measured experimentally and their comparison to simulated sorption isotherms utilizing the models of two reference states built from experimental input.

The investigated polymer/gas systems were selected with respect to application aspects of gas separation. The permeation of gaseous penetrants through polymeric membranes is a rather complex process, involving a gas mixture and a steady-state concentration gradient through the membrane. Properties of the membrane material and its changes as well as transport properties of the gases are therefore not easily attributed to individual phenomena. The fundamental processes of penetrant sorption, transport (diffusion) and relaxation of the matrix underlying the gas separation are, with regard to the combined analysis of experiment, phenomenology and simulation, better investigated utilizing sorption and dilation isotherms of single gases. Here, the step by step procedure of increasing the pressure allows a thorough kinetic analysis and the determination of (quasi-) equilibrium conditions.

Six polymer/gas systems were selected for investigation in this work. CO_2 and CH_4 were selected as penetrant gases because of their vital roles in industrial applications and because of their differing molar, thermodynamic and plasticization properties. Polysulfone (PSU) is a widely investigated conventional glassy polymer with regard to CO_2 sorption [27–33]. and can therefore be used to validate the experimental procedures used in this work. Polymers of the class of 6FDA-polyimides, generally exhibiting a larger *free volume* than PSU, are known to show excellent transport and solubility characteristics with respect to gas separation applications. They furthermore tend to be susceptible to plasticization [34], making the 6FDA-TrMPD (PI4) an ideal choice for the desired investigations. Different *free volume* characteristics may be expected to be present in *polymers of intrinsic microporosity* (PIMs). This new class of polymers, with structures of varying degree of order, shows promising features which have yet to be fully investigated [35–38]. especially with respect to gas sorption properties. For this study the amorphous, membrane forming polymer PIM-1 was selected [39]. It has to be noted that for this polymer different states depending on the sample preparation and history have been identified [40], cf. our preparation described in Section 2.1.1. In contrast to other simulation studies addressing membrane properties (e.g., for PIM-1[41,42]), we attempt to describe the sorption behavior over a wide range of pressures up to 50 bar taking into account the swelling induced by the pentrant molecules.

2. Experimental

2.1. Materials

2.1.1. Sample preparation

Commercial poly(sulfone) (Ultrason S) was obtained from BASF AG, Germany, as a melt extruded film of 100 μm thickness. DSC-measurements at 10 K/min showed non-crystallinity and