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DESIGN OF POLYMERIC MEMBRANES - MODELING AND SIMULATION DIFFUSION STUDIES OF SMALL GAS MOLECULES IN POLYMERIC MATERIALS
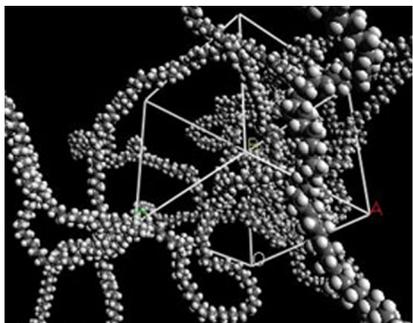
Gas diffusion in polymer membranes and in packageing is a critical property that designers need to model. Materials Studio provides these parameters from atomistic and meso-scale simulations.

Modules used

Materials Studio

• Amorphous Cell
• COMPASS
• Discover

Industry sectors

• Chemicals
• Packaging
• Fuel Cells

Modeling and simulation tools have recently been successfully used to estimate the diffusion mechanism of small gas molecules in polymeric materials. There is an industrial demand for such information, i.e. in the packaging industry and in the design of selective membrane for separation technology. Reliable computational prediction of transport properties of small molecules in polymers is a valuable tool in designing appropriate materials.

Reporting in Journal of Chemical Physics,[1] the researcher demonstrates that molecular dynamics (MD) can be accurate enough to predict the self-diffusion coefficient of small gas molecules in amorphous polymeric materials. As the current method and potentials are validated (against published experimental results), the same method and potentials can be used for the study of novel polymeric materials without having to conduct the experiment (or to synthesize the polymer itself) which can be long and costly, thus making MD a valid tool beside experimental methods.

Different configurations of the polymer chains were generated and placed in a cubic box using the Amorphous Cell module of

the Materials Studio® suite of software. To estimate the density of the material for an infinite chain length, models of increasing chain lengths have been simulated ($[CH_2$-$CH=CH-CH_2]n$, with n = 4,6,8, and 30) and the density computed using 200 ps of NPT molecular dynamics. The 'calculated' density of amorphous cis-polybutadiene is the extrapolated density considering an infinite chain. *(See Figure 1)*. This method has previously been successfully employed on polyetheroxides.[2] To model the gas diffusion, four solute molecules (of N_2, O_2, Ar, CO, and CH_4) were placed in the center of the box containing 10 chains of 30 monomers of polybutadiene.

Equilibration was ensured by following a temperature cycle protocol: a stepwise procedure of constant pressure molecular dynamics (NPT) cycles of heating and cooling (from 400 K to 250 K by steps of 25 K), each of 5-10 ps. 2-3 cycles were performed. This was followed by simulation runs of NPT MDs of 0.2 to 0.5 ns at a given temperature (250 to 400 K) and a pressure of 1 bar. A time-step of 1 fs was employed. The potential and kinetic energies are plotted as a function of time and it is verified that they fluctuate randomly about constant mean values. Moreover, the calculated density *(Fig. 1)* and cohesive energy density *(Fig. 2, as expressed by the solubility parameter)* are compared for the temperature range to that of experimental work. The production runs consisted of 3 ns of NVT dynamics at each temperature of simulation (250, 275, 300, 325, 350, 375, and 400 K). A time-step of 3 fs was employed.

Table 1 summarizes the results of the computation of the diffusion coefficients of the small gas molecules in PBD at room temperature as calculated.

	Ar	O_2	N_2	CO_2	CH_4
(1) Exp. (298 K) ref. 4	4.06	1.5	2.96	1.05	-
(2) Calc. (300K) ref. 1	7.03	9.5	8.8	5.3	7.5
(3) Calc. ref. 3	-	-	-	-	2.25

Table 1. *Estimated and Experimental Diffusion Coefficient for Ar, O_2, N_2, CO, and CH_4 in amorphous* **cis**-*PBD[a]*
[a] Units of Diffusion Coefficients, D (10-6 cm2/s).

Comparison with experimental data at 298K reveals a small overestimation of the diffusion coefficients attributed to an inexact free volume distribution and to an overestimation of the polymer flexibility related to the limited chain length. Fig. 3 reports a comparison of the calculated diffusion coefficient of methane at various temperatures with data from ref. 3. The decrease of the activation energy with the temperature is clear in both cases. This effect is attributed to a gradual change in the diffusion mechanism of the gas molecule as temperature varies. At low temperature, the polymer chains move very
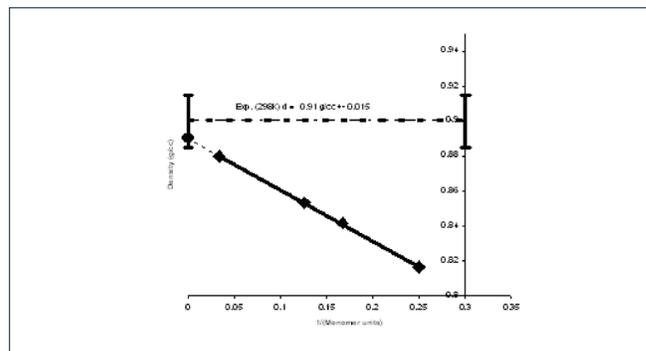
Fig. 1. *Density variation as a function of polymer chain length. Diamonds: Average MD results of 3 simulations; dot: projected results for infinite chain length using a linear regression from MD results at lower chain length; dash line: experimental data.[4]*
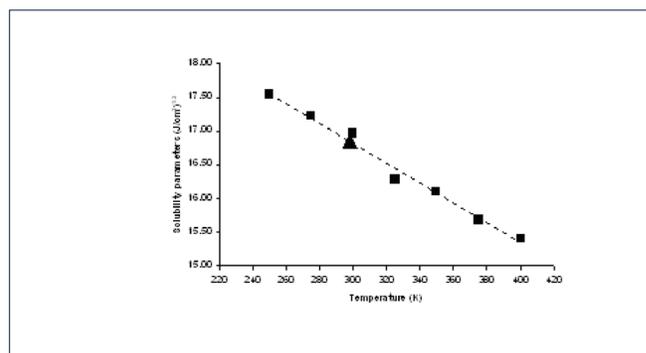
Fig. 2 *cis-PBD solubility parameter variation with Temperature. Filled squares, this work; triangles, experiment.[4] The line is a guide to the eye.*
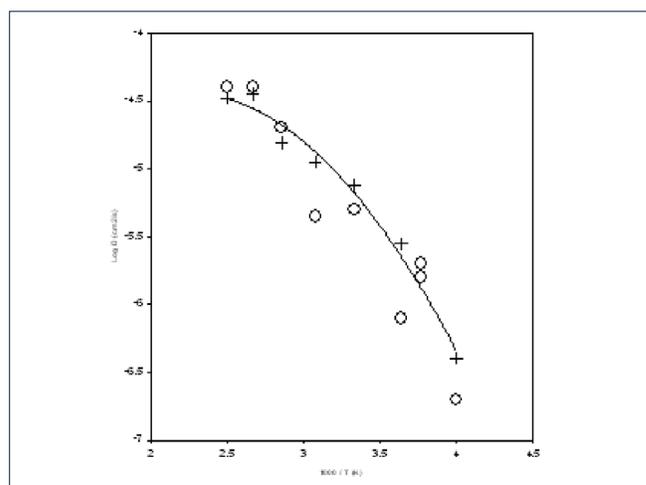
Fig. 3 *Arrhenius plot of the diffusion coefficients of methane and second order polynomial fit. Crosses and line fit, this work; circles.[3]*

little, therefore the channels formed between the micro-voids are rare. Moreover, the density is higher and the number and volume of those micro-voids is minimal. Consequently the number of (effective) jumps of the gas molecule is small.

The diffusion mechanism is found to change at low temperature from a pure hopping mechanism to a more liquid like behavior at high temperatures as indicated by the change of slope of the Arrhenius plots. *(Fig. 3)*

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