



## ENABLING SCIENCE

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# Exploiting entropy to separate alkane isomers

## Molecular packing efficiencies and preferential adsorption can separate branched and straight-chain alkanes.



Recent changes in the specifications for reformulated gasoline, requiring reduction in the benzene content, have increased the refining industry's need for catalytic isomerization to convert straight-chain hydrocarbons to branched hydrocarbons. Branched hydrocarbons are preferable to straight-chain hydrocarbons as ingredients in gasoline because they burn more efficiently and have a higher octane number ([1](#)).

We discuss a new separation principle for separating isomers of alkanes in the  $C_4$ – $C_8$  range by adsorption on silicalite, a microporous form of silica. The normal alkanes are preferentially adsorbed because of configurational entropy effects; they “pack” more efficiently within the channel structures of silicalite. The entropy-based separation principle has considerable commercial potential.

Consider, for example, the isomers of hexane: *n*-Hexane has a research octane number (RON) of 30, whereas the corresponding RON values for its isomers are as follows: 2-methyl pentane (2-MP) = 74.5; 3-methylpentane (3-MP) = 75.5; 2,2-dimethylbutane (2,2-DMB) = 94; and 2,3-dimethylbutane (2,3-DMB) = 105. In the catalytic isomerization process, straight-chain hydrocarbons are converted to their mono- or di-branched structures. However, the product of catalytic isomerization is a mixture of linear and branched hydrocarbons that are in thermo-dynamic

equilibrium, and the separation of linear hydrocarbons from their branched isomers becomes necessary.

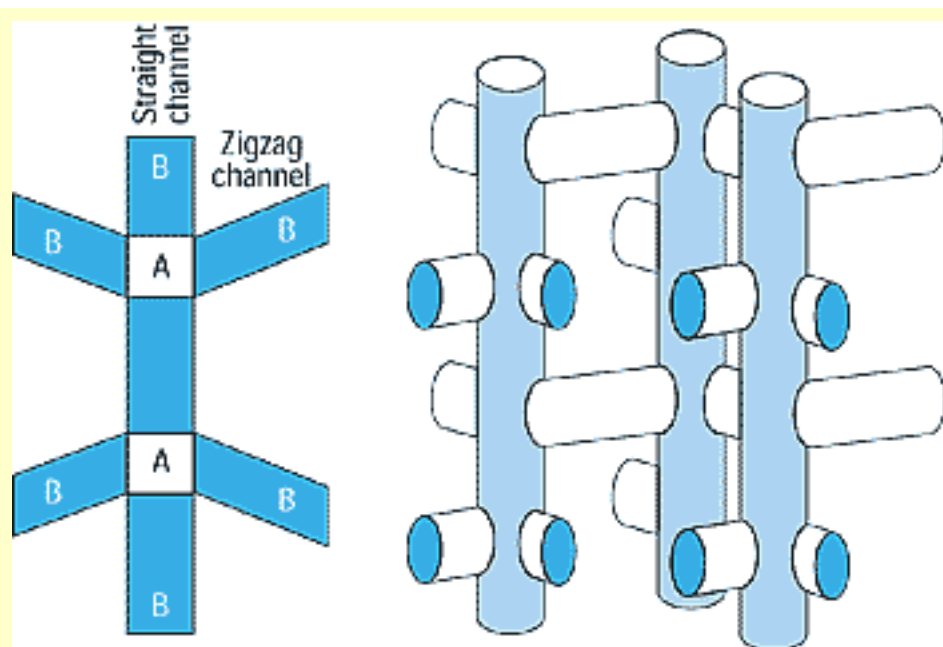
Hydrocarbon isomers are usually separated by adsorption in a bed of zeolite 5A particles (2). The principle of separation is molecular sieving. Only the linear paraffin is capable of entering the pores of zeolite 5A (calcium-substituted  $\text{NaAlSiO}_4$ ), and the branched isomers are excluded. One important disadvantage of adsorption separation using zeolite 5A is that the diffusivities—and hence the fluxes—are very low, necessitating large quantities of the zeolite and thus large processing equipment.

We discuss and develop a new separation principle for the adsorption and separation of hydrocarbon isomers, using silicalite as the sorbent and taking advantage of subtle configurational entropy effects. We consider the specific example of the separation of the isomers of hexane. This mixture is of particular interest because the components are important constituents of gasoline. We also discuss how the entropy principle can be applied to the separation of other hydrocarbon mixtures.

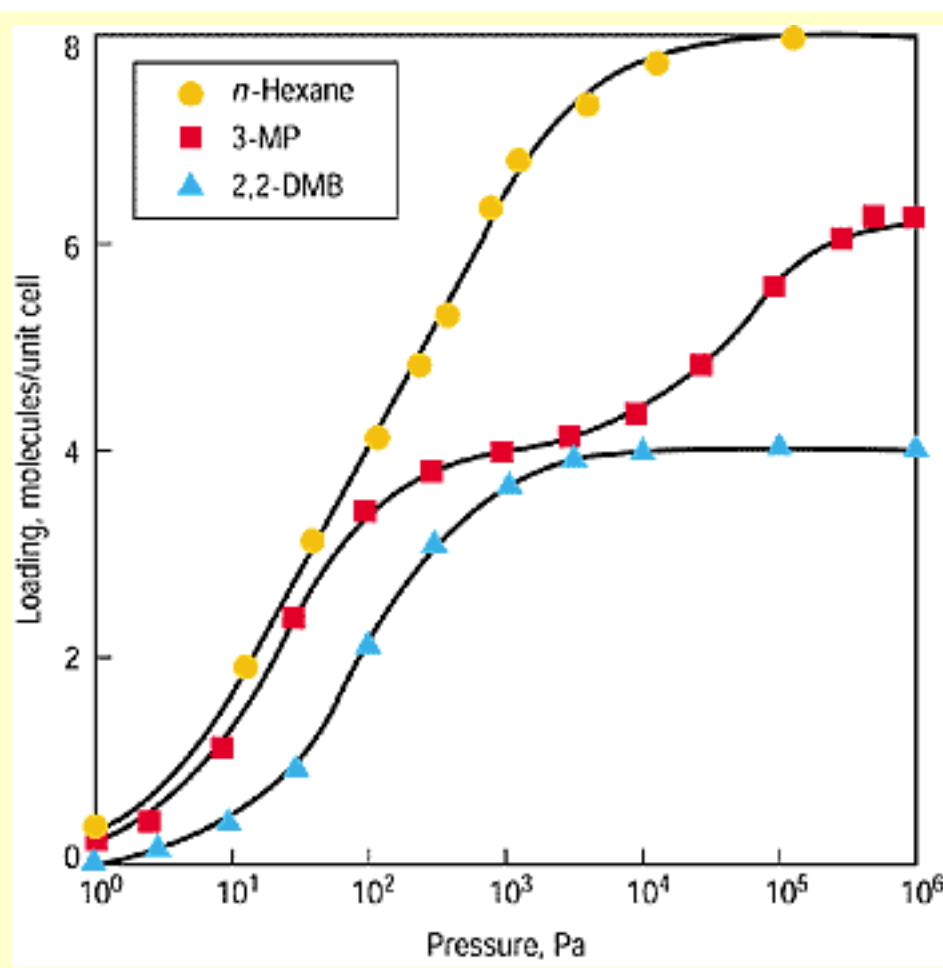
### Configurational entropy effects on adsorption

A careful examination of the physical properties of linear and branched alkanes (3) shows that the largest difference between these isomers is related to the freezing point. For example, when a mixture of *n*-hexane and 2-MP is cooled, the crystals of the linear isomer will be the first to form. The reason is that the linear paraffin molecules stack more easily. Branching destroys the symmetry required for crystal formation. In other words, the difference in the freezing points is due to differences in ordering or packing efficiencies. The major drawback in applying this principle to separate linear and branched alkanes is that the mixtures must be cooled to very low temperatures, on the order of 120–180 K. Therefore, crystallization by freezing is not a practical solution for separation of isomers in the  $\text{C}_4$ – $\text{C}_8$  range for use as blending components for gasoline.

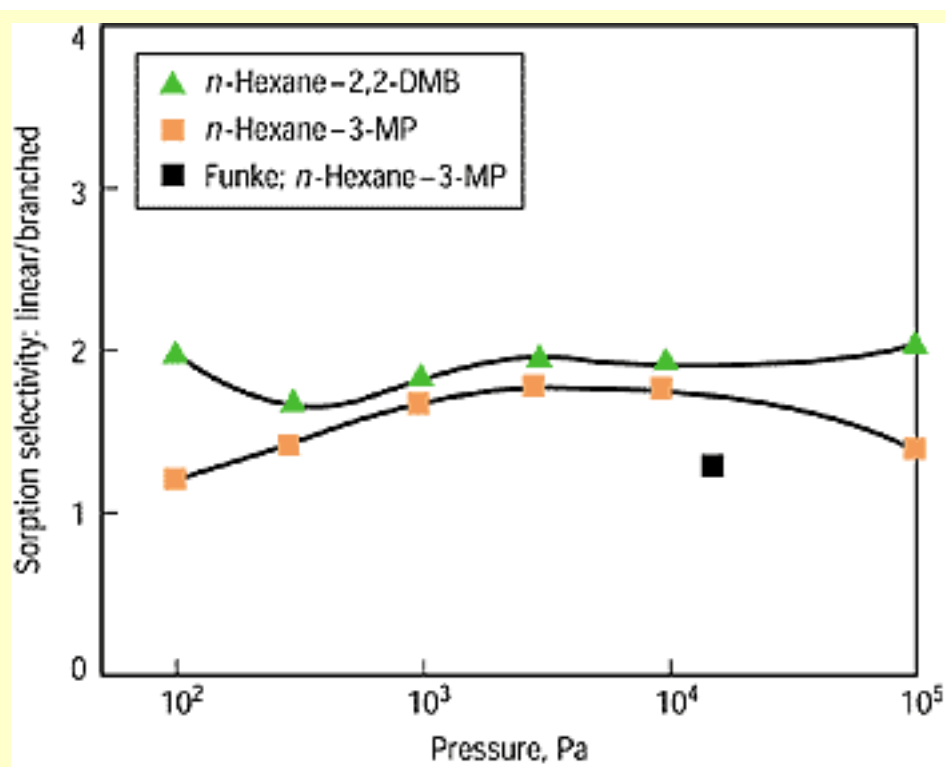
Ideally, we would like to be able to exploit packing efficiency, or configurational entropy, differences without the need to cool to such low temperatures. To achieve this goal, we consider adsorption of the hexane isomers inside the matrix of an ordered structure, such as silicalite (Figure 1). Silicalite consists of straight channels and zigzag channels, which cross each other at intersections. The length of the normal hexane molecule is commensurate with the length of the straight channel between two intersections (4). The differences in the saturation loadings,



**Figure 1. Schematic of the silicalite structure** indicating the channel intersections (A) and channel interiors (B) consisting of straight and zigzag channels.



**Figure 2. Pure component isotherms** for *n*-hexane, 3-methylpentane (3-MP), and 2,2-dimethylbutane (2,2-DMB) at 89 °C in silicalite. The isotherms were determined by configurational-bias Monte Carlo simulations ([8–11](#)).



**Figure 4. Sorption selectivity for separation of hexane isomers**, calculated using pure component isotherm data at 89 °C. The experimental permeation selectivity for *n*-hexane-3-MP obtained by Funke et al. ([12](#)) is also shown.

expressed in molecules per unit cell, between linear and branched alkanes in silicalite result from the more efficient packing of the linear hexane molecules. Figure 2 shows the pure component isotherms at 89 °C. The pure component isotherm data are available in the literature ([5–11](#)). The maximum loadings for hexane isomers (molecules per unit cell) are 8 for *n*-hexane, 6.3 for 3-MP, and 4 for 2,2-DMB. This means that for adsorption of pure components at equilibrium, the maximum loadings of 2,2-DMB would be half that of *n*-hexane.

We also note from Figure 2 that the isotherm for 3-MP exhibits an inflection at a loading of 4 molecules per unit cell. The inflection in the isotherm is due to the preferential location of 3-MP at the intersections, as evident in the snapshot in ([Figure 3](#)), which was obtained by using molecular simulation techniques ([8](#)). However, at a loading of 4 molecules per unit cell, all the intersections are fully occupied. To obtain

loadings higher than 4, these molecules must seek residence in the channel interiors, which requires more energy. This leads to an inflection in the isotherm. The 2,2-DMB molecule behaves much the same way, but the extra push required to place these molecules is so large that the maximum loading is only 4 molecules per unit cell.

The adsorption selectivity, defined as the ratio of the loadings of linear to branched alkane, determined from the pure component isotherms is shown in Figure 4. Funke and co-workers, who performed permeation experiments using a silicalite membrane for the components *n*-hexane and 3-MP, found the permeation selectivity to be 1.3 ([12](#)). Their measurement data are also plotted in Figure 4 and agree with the sorption selectivity calculations. The selectivity values are  $<2$  and not high enough to be of commercial interest.

### CBMC mixture simulations

Although there is a considerable amount of published experimental data on pure component isotherms for various hydrocarbons on silicalite, very little data exist for mixture isotherms. This lack of data is most probably due to the difficulty of experimentation. At present,  $>100$  zeolite structures are known, so a major effort will be needed to measure all relevant pure component isotherms. We can expect to have a very small fraction of experimental data for all possible mixtures. It is therefore essential to have an efficient method to estimate mixture isotherms reliably.

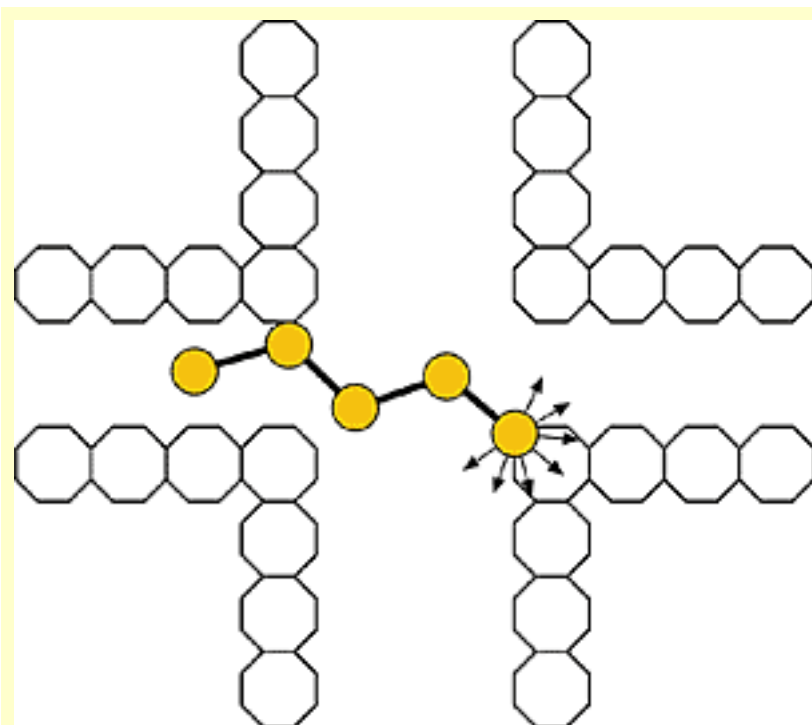
Our approach is to calculate mixture isotherms using configurational-bias Monte Carlo (CBMC) simulations. These are performed in the grand-canonical ensemble, in which the zeolite is in contact with a reservoir that fixes the chemical potential of each component and the temperature of the system. The advantage of the grand-canonical ensemble is that one can use an infinitely large zeolite crystal. The molecules “enter” the zeolites via Monte Carlo steps in which particles are created or annihilated. Thus, the simulations are not dependent on the diffusion of molecules from the gas phase into the zeolite. In a conventional grand-canonical ensemble simulation, the particles are inserted at a random position. For methane, this is a successful approach. For octane, however, in almost all cases, at least one atom of this molecule is inserted on top of a zeolite atom; and such a high-energy configuration will always be rejected in a Monte Carlo simulation. The CBMC technique has been developed to solve this problem.

With this technique, we grow a flexible alkane molecule atom by atom in such a way that the “empty spaces” in the zeolite are found (Figure 5). The bias of this growing scheme is removed by a modification of the “acceptance rules”, which must be obeyed for a successful “move” (8). The acceptance ratio of the particle exchange move

is increased by a factor of 10–100 and thus makes these simulations possible. In the simulations presented in this work, the linear and branched alkanes are described with a united-atom model; that is, CH<sub>3</sub>, CH<sub>2</sub>, and CH groups are considered as single interaction centers. The zeolite is assumed to be rigid, and the interactions of the alkane with the zeolite are dominated by the oxygen atoms of the zeolite. The alkane–zeolite and alkane–alkane interactions are described by a Lennard–Jones potential. The intramolecular interactions include bond-bending and torsion potentials as well as a fixed C–C bond length. The force-field parameters and the details of the simulations are reported by Vlugt and co-authors (8).

Our simulation box consists of 16 ( $2 \times 2 \times 4$ ) unit cells of silicalite. The simulations take place in cycles, and in each cycle an attempt is made to perform one of the following moves:

- displacement of a chain: a chain is selected at random and given a random displacement;
- rotation of a chain: a chain is selected at random and given a

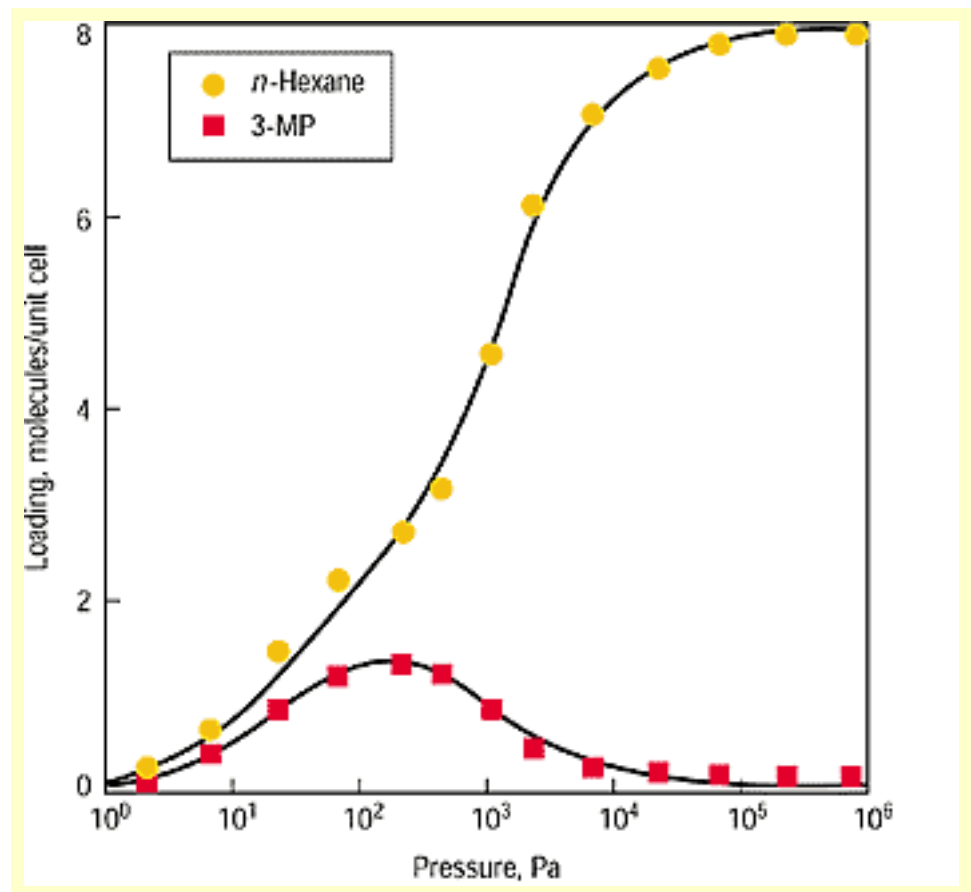


**Figure 5. Schematic of the growing of an alkane in a zeolite in a CBMC “move”.** The octagons represent the atoms of the zeolite, and the circles represent the atoms of the alkane. Four atoms have been inserted successfully, and an attempt is made to insert the fifth.

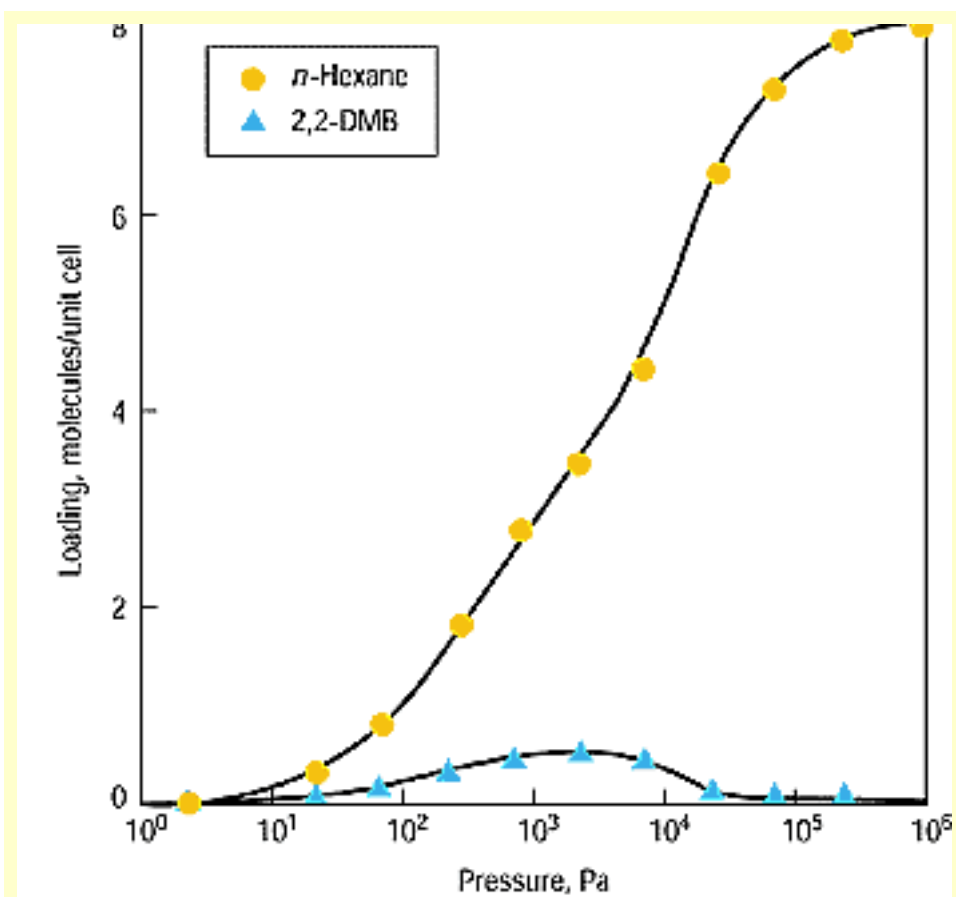
random rotation around the center of mass;

- partial regrowing of a chain: a chain is selected at random, and part of the molecule is regrown using the CBMC scheme;
- exchange with reservoir using the CBMC scheme: it is decided at random whether to add or to remove a molecule from the zeolite; and
- change of identity (only in the case of mixtures): one of the components is selected at random, and an attempt is made to change its identity ([8](#)).

A total simulation consists of at least 300,000 Monte Carlo cycles.

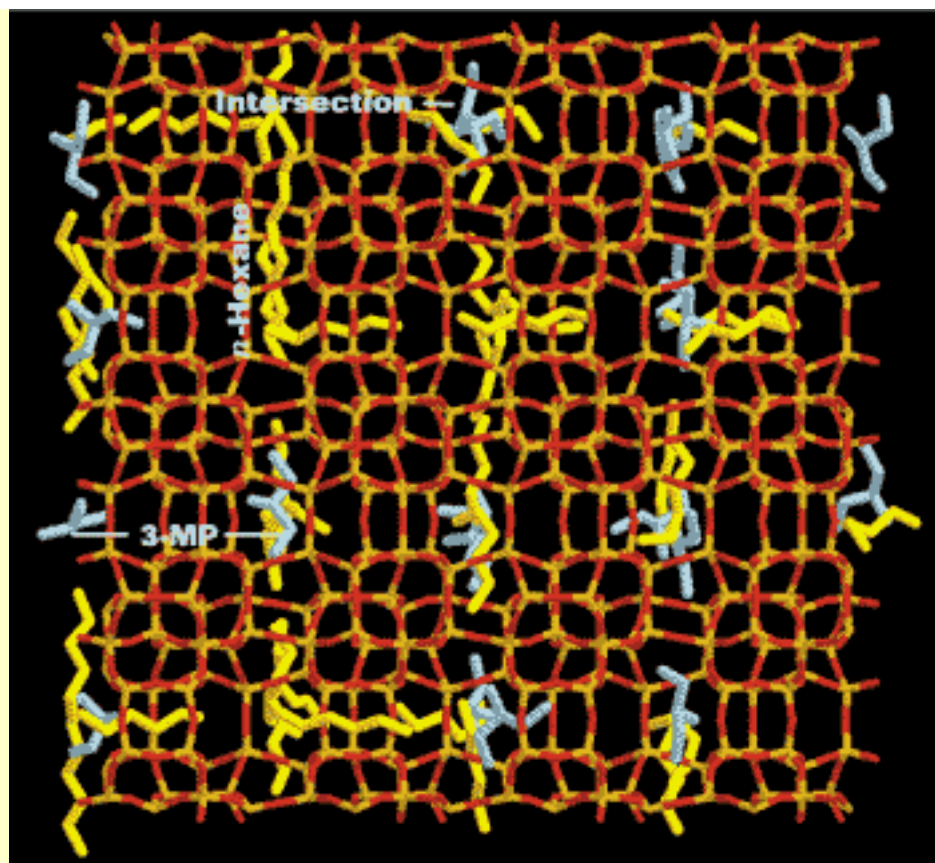




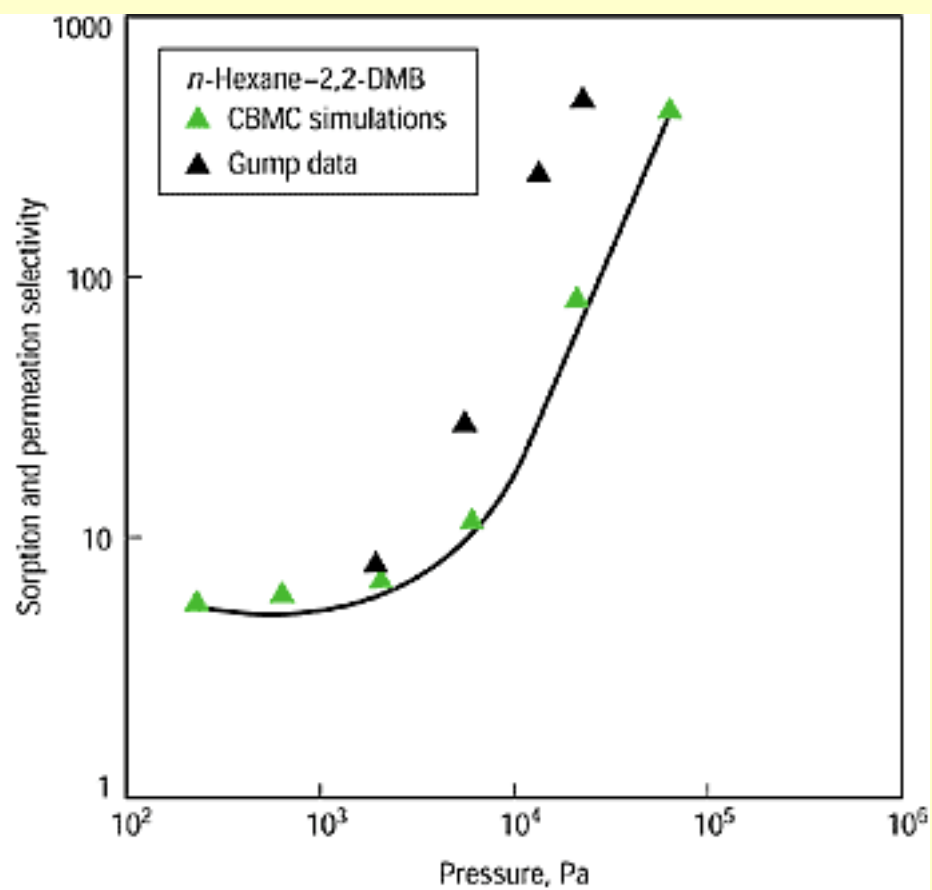
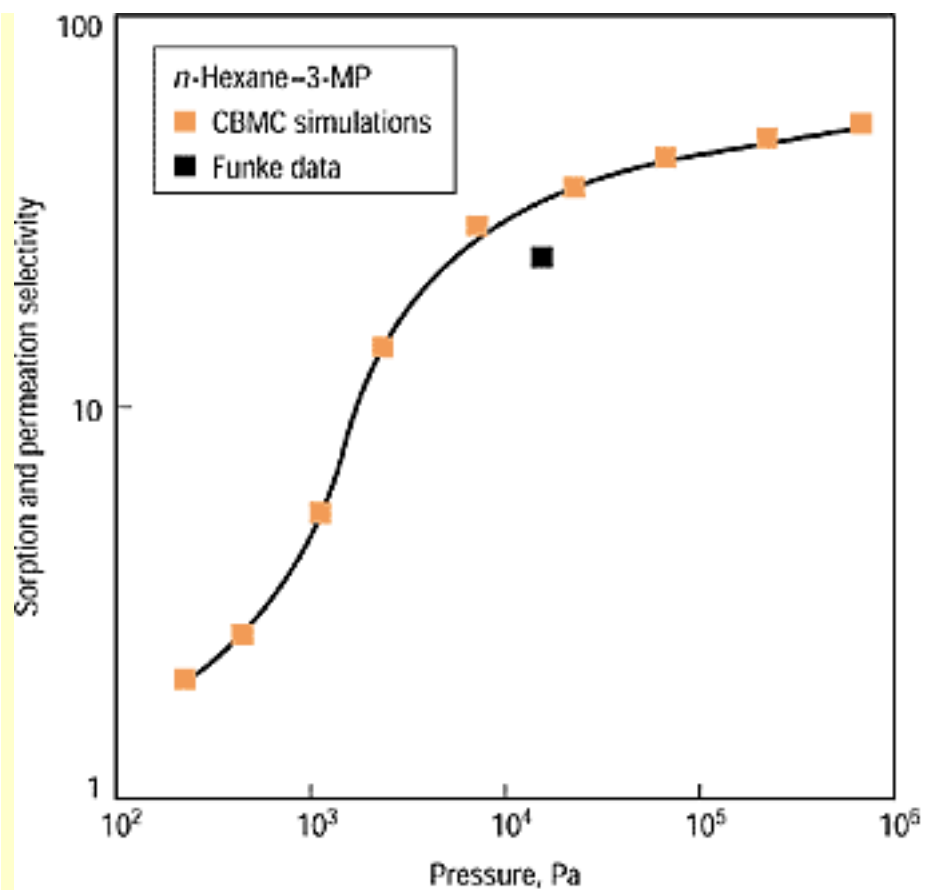


**Figure 6. Loadings for 50:50 mixtures of *n*-hexane–3-MP at 89 °C (top) and *n*-hexane–2,2-DMB at 125 °C (bottom) in silicalite.**





**Figure 7. “Snapshot” showing the locations of *n*-hexane and 3-MP** from a 50:50 mixture in silicalite at 89 °C and 100 Pa. The preferential siting of 3-MP (light blue molecule) at the intersections between the straight and zigzag channels is evident in this side view. The linear alkane (yellow) can be located at any position within the structure.



**Figure 8. Sorption selectivities for the separation of hexane isomers, calculated using CBMC mixture simulations.** The experimental permeation selectivities of these mixtures obtained by Funke et al. ([12](#)) and Gump et al. ([13](#)) are also shown.

Consider the simulated isotherm for a 50:50 mixture of *n*-hexane–3-MP at 89 °C. The branched alkane 3-MP exhibits a curious maximum with respect to molecular loading (Figure 6, top). As the partial pressures increase to 100 Pa, the sorbate loading of both linear and branched alkanes increases until a maximum is reached in the loading of 3-MP. This occurs at a total mixture loading of 4 molecules per unit cell. Up to this point, there is really no competition between *n*-hexane and 3-MP; both are almost equally easily adsorbed.

Examination of a snapshot of the molecular sitings at 100 Pa shows that all the 3-MP molecules are located at the intersections between the straight channels and the zigzag channels, whereas *n*-hexane molecules are located everywhere (Figure 7). The *n*-hexane molecules fit nicely into straight and zigzag channels ([4](#)); these molecules have a higher packing efficiency than 3-MP. As the pressure is increased beyond 100 Pa, it is more efficient to obtain higher loading by replacing the 3-MP with *n*-hexane; this configurational entropy effect is the reason behind the curious maximum in the 3-MP isotherm.

For the mixture *n*-hexane–2,2-DMB, a similar result is obtained at higher pressure (Figure 6, bottom). Again we note the curious maximum in the 2,2-DMB loading when the mixture loading corresponds to 4 molecules per unit cell.

From the mixture isotherms shown in Figure 6, it is clear that high selectivities for separation of linear and branched alkanes can be obtained if the conditions inside the zeolite correspond to those on the right side of the “mountain”, or loading peak, of the branched isomer in the 50:50 mixture. The sorption selectivities, as well as the experimentally determined permeation selectivities by Funke and co-workers ([12](#)) and Gump and co-workers ([13](#)), are shown in Figure 8. There is excellent agreement between the selectivities determined from CBMC simulations and those of the experimentally determined membrane permeation. The experimental data verify the entropy-driven separation concept.

## Pentanes and heptanes

The generic character of the entropy-driven separation principle is demonstrated by applying it to pentane and heptane isomers. We performed CBMC simulations of 50:50 mixtures of pentanes (*n*-pentane and 2-methylbutane) and heptanes (*n*-heptane and 2-methylhexane) at their respective boiling points, 37 and 101 °C. The results shown in [Figure 9](#) display the same qualitative features as for the hexane isomers; the table mountain maximum for 2-methylhexane is striking. High selectivities are obtained at pressures in the 10-MPa region for separating the heptane isomers. In this case, the membrane permeation device is best operated in the pervaporation (permeation–evaporation) mode, in which the upstream compartment is in the liquid phase and the downstream compartment is in the vapor phase ([14](#)).

Configurational-entropy effects can be exploited to obtain high sorption selectivities in the separation of linear from branched alkanes when silicalite is used as the sorbent. This novel concept holds considerable promise in practice. CBMC simulations are powerful tools for predicting the sorption isotherms and for determining the right process conditions for maximum separation selectivity. In addition to alkane isomer separations using silicalite, the CBMC techniques can also be used for other compounds and for other zeolitic structures ([15](#), [16](#)).

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