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Computational Physics in Petrochemical Industry

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Abstract

Recent progress in the simulation of complex fluids is reviewed. It is shown that the use of recently developed Monte Carlo techniques allows the simulation of systems that several years ago were considered impossible to study via molecular simulations only. It is now possible to apply simulation techniques, which used to be limited to systems containing small molecules, to systems which are of interest for petrochemical applications. In this review, this development is illustrated by two examples of practical importance: the adsorption of alkanes in zeolites and the phase behavior of long-chain alkanes.

1. Introduction

The title may suggest that molecular simulations in academia are different from those performed in industry. In most cases the basic simulation techniques are the same, but the aims will in general be different. The aims for which simulations are performed in industry impose some boundary conditions that may require special attention. For example, in academia it is good practice to perform a simulation on the simplest system available. The reasons are obvious, for such a system a simulation is relatively easy to implement and for those systems ample experimental data is usually available. If such a simulation has been performed successfully, does this imply it can be used in an industrial context? The answer, inspired by the increasing pressure to do "relevant" science, will probably be yes!

In an industrial context, however, one normally does not have the possibility to select the simplest system. The molecules that have to be simulated are dictated by business objectives rather than scientific convenience. Of course, one can always argue that once the reliability of the underlying basic principle have been demonstrated, it is a matter of applying these principles to more complex systems. In some cases it may indeed be as simple as that, in particular if the computers are sufficiently powerful to deal with these more complex systems in a reasonable amount of time. For some problems, however, the increase in computer time can be prohibitively large; it may take many years of super-computer time before a calculations is finished. For those type of systems it is important that novel algorithms will be developed.

Let me illustrate the above with a specific example we have been working on the last few years; the adsorption of alkanes in the pores of a zeolite. Zeolites are porous materials which are used as catalysts in petro-chemical applications. A prerequisite for an understanding of the catalytic activity of these zeolites is a knowledge of the behavior of the molecules adsorbed in the pores of these zeolites. Since this type of information is extremely difficult to obtain experimentally, simulations appear to be an attractive alternative [1]. Indeed, over the last decade many simulation studies on the behavior of molecules in zeolites have been published (for a review see Ref. [2]). A more careful look at these studies reveals that most simulations concern the adsorption of noble gases or methane [3], only a few studies of ethane or propane [4] have been published. The reason why only small molecules have been studied becomes clear from the work of June *et al.* [5] and Hernández and Catlow [6], in which molecular dynamics simulations were used to investigate the diffusion of butane and hexane in the zeolite silicalite. June *et al.* showed that the diffusion of butane from one channel of the zeolite into another channel is very slow compared to diffusion of bulk butane. As a consequence many hours of super-computer time were required to obtain reliable results. In addition, since the diffusion coefficient decreases significantly with increasing chain length, extrapolation of these results suggests that many years of super-computer time would be required to obtain comparable results for the longer alkanes.

The above example illustrates one of the main limitations of Molecular Dynamics. In such a simulation, the approach is to mimic the behavior of the molecules as realistically as possible. If successful, all properties will be like in nature, including the diffusion. If the molecules diffuse slowly this will be reflected in very long simulation times and in the case of long chain alkanes these simulation times turned out to be much longer than we can currently afford. In principle, one can circumvent this intrinsicly slow dynamics by using a Monte Carlo technique. In a Monte Carlo simulation one does not have to follow the "natural path" and one can, for example, perform a move in which it is attempted to displace a molecule to a random position in the zeolite. If such a move is accepted, it corresponds to a very large jump in phase space.

Again, utilization of these type of un-natural Monte Carlo moves turned out to be limited to small molecules. For example, Goodbody *et al.* [7] have used this Monte Carlo trick to determine the adsorption isotherm of methane in silicalite. In such a simulation one can observe that out of the 1000 attempts to move a methane molecule to a random position in the zeolite 999 attempts will be rejected because the methane molecule overlaps with a zeolite atom. If we were to perform a similar move with an ethane molecule, we would need 1000 × 1000 attempts to have one that was successful. Clearly, this random insertion scheme will break down for any but the smallest alkanes.

The above example the adsorption of chain molecules in the pores of a zeolite is used to illustrate the problems that may occur if one uses a conventional simulation techniques to more complex systems. Similar problems may occur in the simulation of phase equilibria of chain molecules [8] and simulations of polymers [9]. To be able to use these techniques to these complex systems it is therefore important to develop novel algorithms. To allow for the simulations of these complex systems within an industrial context these algorithms should be many orders of magnitude more efficient than the conventional algorithms.

2. Simulation techniques

To make Monte Carlo moves of long chain molecules possible, Siepmann and Frenkel [10] have developed the configurational-bias Monte Carlo technique for lattice models. This technique is based on the early work of Rosenbluth and Rosenbluth [11] and Harris and Rice [12]. This technique has since been extended to continuum models by Frenkel *et al.* [13] and de Pablo *et al.* [14].

The starting point for configurational-bias Monte Carlo is the scheme as introduced by Rosenbluth and Rosenbluth in 1954 [11]. At first sight, this may not appear to lead to a new algorithm but to a very old one. The original Rosenbluth scheme itself was designed as a method to sample polymer conformations. The original Rosenbluth scheme, however, suffers from the drawback that it generates an unrepresentative sample of all polymer conformations, i.e. the probability to generate a particular conformation using the Rosenbluth scheme, is not proportional to its Boltzmann weight. Rosenbluth and Rosenbluth introduced the weight W to correct for this biasing in the computation of thermal averages. Batoulis and Kremer [15] have shown that this correction procedure only works for unrelatively short chains. The solution of this problem is to un-bias the Rosenbluth sampling in such a way that the correct (Boltzmann) distribution of chain conformations is generated in a Monte Carlo sequence. In the configurational-bias scheme, the Rosenbluth weight is used in the acceptance rule of trial conformations that are generated with the Rosenbluth procedure. If one were to use the ordinary Metropolis acceptance rule, such a bias in the configurations of the molecules would lead to an incorrect distribution of configurations. Frenkel *et al.* [13] have shown that by using acceptance with the Rosenbluth weight this bias can be removed exactly. As a consequence, all conformations are generated with their correct Boltzmann weight. This removes the main drawback of the original Rosenbluth scheme.

At this point it is important to emphasize that this is a Monte Carlo technique and therefore cannot be used directly to determine transport properties. One may consider using the configurational-bias Monte Carlo technique to enhance the equilibration, but to determine the transport properties one has to do a molecular dynamics simulation. For cases in which the interest is primarily in the thermodynamic properties, the configurational-bias Monte Carlo technique can be extremely useful since it can be many orders of magnitude more efficient than the conventional techniques.

The configurational-bias Monte Carlo technique can be used in ordinary NVT Monte Carlo Carlo simulations [13, 14, 16–18], but can also be combined with the grand-canonical ensemble [19] and with the Gibbs-ensemble technique [20–22].

In the next section the use of the CBMC technique is illustrated with some examples of practical relevance.

3. Applications

3.1. *Adsorption of alkanes in zeolites*

In the introduction we have used the adsorption of molecules as an example to illustrate the type of problem one can encounter in simulating systems that exhibit slow diffusion. Smit and Siepmann have used the configurational-bias Monte Carlo technique to study the energetics and siting of alkanes in the zeolites silicalite and mordenite [18, 23]. In these simulations alkane molecules are modelled with a united atom model, i.e. a CH_3 and a CH_2 group are considered as a single interaction centre and the zeolite is modelled as a rigid crystal. The zeolite-alkane interactions are assumed to be dominated by dispersive interaction with the oxygen atoms, which are described with a Lennard–Jones potential. A closely related technique was used by Maginn *et al.* [24]. Figure 1 shows that the simulations of Smit and Siepmann and Maginn *et al.* predict heats of adsorption of the longer chain alkanes in silicalite that are in good agreement with the experimental data and the simulations of Bigot and Peuch [25].

Simulations can also be used to determine adsorption isotherms. Adsorption isotherms are of practical importance since they give information on the number of molecules adsorbed in the pores of a zeolite as a function of the pressure of the reservoir. Adsorption isotherms are also of fundamental interest since they may signal phase transitions, such as capillary condensation or wetting, of the fluid inside the pores [26]. For example, if a system exhibits capillary condensation, one would measure a stepped adsorption isotherm with hysteresis. Steps or kinks without hysteresis are occasionally observed on flat substrates [27]. Since the pores of most zeolites are of molecular dimensions, adsorbed alkane molecules behave like a (pseudo) one-dimensional fluid. In a one-dimensional system phase transitions do not occur and therefore one would expect that for alkanes the adsorption isotherms are of type I, i.e. do not show kinks or steps. If steps occur they are usually attributed to capillary condensation in the exterior secondary pore system formed by the space between different crystals

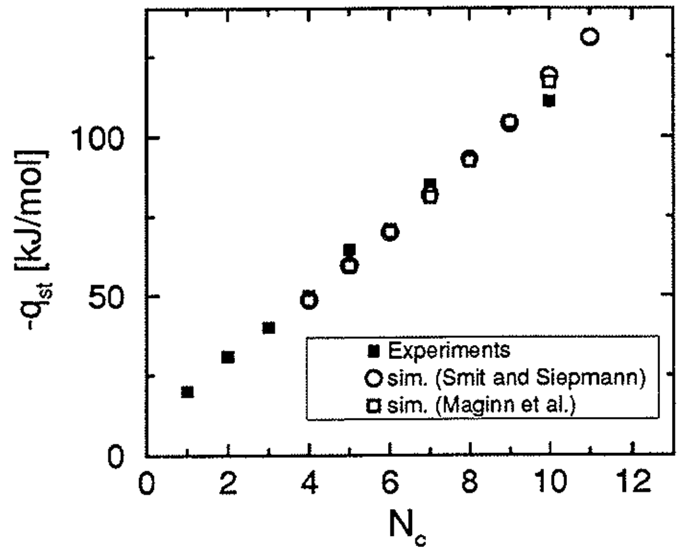

Fig. 1. The heats of adsorption of the alkanes in silicalite as a functior the total number of carbon atoms. The experimental data are compiled from Refs [28, 31, 49–52] and the simulation data are form Maginn *et al.* [24] and Smit and Siepmann [18, 23].

[28]. For silicalite, adsorption isotherms have been determined for various n-alkanes: for the short chain alkanes methane–pentane) the isotherms are indeed of type I [28, 29], also for decane a type I isotherm is observed [28, 30]. For hexane and heptane, however, a kink or step is observed [29, 31].

Adsorption isotherms are conveniently determined from simulations in the grand-canonical ensemble. In this ensemble the temperature and chemical potential are imposed, but the number of particles is allowed to fluctuate. Adsorption isotherms of alkanes in silicalite have been simulated by Smit and Maesen [32]. The simulated adsorption isotherms for hexane and heptane are shown in Fig. 2. The agreement of the simulation results with the experimental data is good at high pressures, but at low pressures deviations exist which indicate that the zeolite-alkane model may be further improved. It is interesting to note that for heptane both the experiments and the simulations show a step at approximately half the loading. Also for hexane detailed inspection of the calculated adsorption isotherm shows a kink at this loading. Since the simulations are performed on a perfect single crystal, these deviations from the type I isotherm must be due to a transition of the fluid inside the pores and can not be attributed to the secondary pore system. Smit and Maesen attribute this transition to a commensurate "freezing" in the channels of a zeolite. The length of a hexane molecule is of the order of the length of the period of the zig-zag channel. At low chemical potential, the hexane molecules move "freely" in these channels and the molecules will be part of their time in the intersections. If part of the intersection is occupied, other molecules can not reside in the straight channels at the same time. At high pressures, almost all hexane molecules are exactly fitting into the zig-zag channel, they do no longer move freely and keep their nose and tail out of the intersection. In such a configuration the entire straight channel can now be tightly packed with hexane molecules. This may explain the plateau in the adsorption isotherm; in order to fill the entire zeolite structure neatly, the hexane molecules located in zig-zag channels have first to be "frozen" in these channels. This "freezing" of the positions of the hexane molecules implies a loss of entropy and will therefore only occur if the pressure (or chemical potential) is sufficiently high to compensate for this loss. Further experimental evidence for this commensurate freezing of hexane and heptane has been found by van Well *et al.* [33].

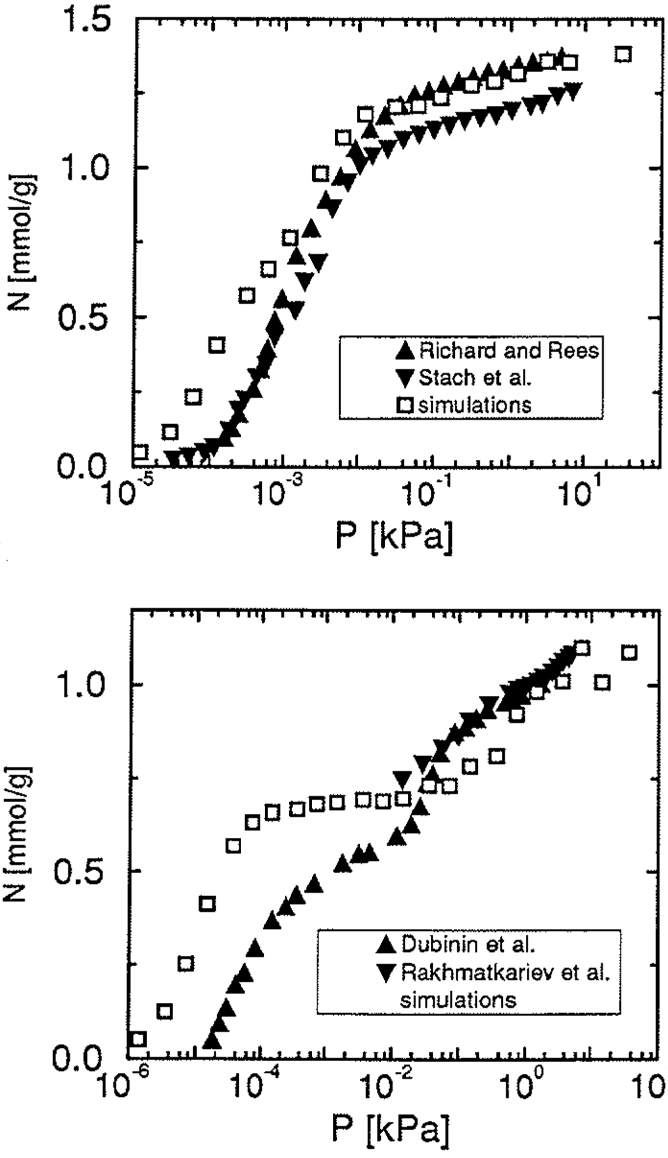

Fig. 2. Adsorption isotherms of hexane (top), and heptane (bottom), the closed symbols are experimental data [29, 31, 53] and the open symbols the results from simulations at $T = 298$ [K].

3.2. *Phase equilibria of n-alkanes*

The Gibbs-ensemble technique was introduced by Panagiotopoulos [34] as an efficient tool to simulate vapor-liquid phase equilibria. In the Gibbs-ensemble scheme simulations of the liquid and vapor phases are carried out in parallel. Monte Carlo rules which allow for changes in the number of particles and the volume, ensure that the two boxes are in thermodynamic equilibrium with each other. Since the two boxes are not in "physical contact", there is no interface and the bulk properties of the two coexisting phases can be obtained directly with a surprisingly small number of particles. This makes the Gibbs ensemble extremely efficient for phase equilibrium calculations. The major limitation of the Gibbs-ensemble technique is that one of the steps involves the exchange of particles between the two boxes. For liquids consisting of small molecules this does not cause serious problems. However, for chain molecules the probability of successful exchanges can become very small. For example, under conditions where it takes approximately 10^3 attempts per successful exchange of methane, it takes of the order of 10^{3n} attempts for an n-alkane. However, by combining the Gibbs-ensemble method with configurational-bias Monte Carlo, the method can be made to work for much longer chain molecules.

Alkanes are thermally unstable above approximately 650 K, which makes experimental determination of the critical point of alkanes longer than decane (C_{10}) extremely difficult. The longer alkanes, however, are present in mixtures of practical importance for the petrochemical industry. In these mixtures, the number of components can be so large that it is not practical to determine all phase diagrams experimentally. One therefore has to rely on predictions made by equations of state. The parameters of these equations of state are directly related to the critical properties of the pure components. Therefore, the critical properties of the long-chain alkanes are used in the design of petrochemical processes, even if they are unstable close to the critical point [35]. Unfortunately, experimental data are scarce and contradictory, and one has to rely on semi-empirical methods to estimate the critical properties [35].

Siepmann *et al.* [22, 36] have used the combination of the Gibbs-ensemble technique and configurational-bias Monte Carlo to simulate vapor-liquid equilibria of the n-alkanes at conditions where experiments are not (yet) feasible. Phase diagrams are very sensitive to the choice of interaction potentials. Most available models for alkanes have been obtained by fitting simulation data to experimental properties of the liquid at standard conditions. In Fig. 3 the vapor-liquid curve of octane as predicted by of some of these models is compared with experimental data. This figures shows that the models of Refs [37, 38] which give nearly identical liquid properties, yield estimates of the critical temperature of octane that differ by 100 K. Siepmann *et al.* [22, 36] used these vapor-liquid equilibrium data to improve the existing models.

In Fig. 4 the critical temperatures and densities as predicted by the model of Siepmann *et al.* are plotted *vs.* carbon number. The simulations reproduce the experimental critical points very well. There is, however, considerable disagreement between the various experimental estimates of the critical densities.

Much of our current knowledge of the critical properties of the higher alkanes is based on extrapolations of fits of the experimental data up to C_8. The most commonly used extrapolations assume that the critical density is a a monotonically increasing function of the carbon-number, approaching a limiting value for the very long alkanes [35, 39]. In contrast to these expectations, the experimental data of Anselme *et al.* [40] indicate that the critical density has a maximum for C_8 and then decreases monotonically. The data of Steele (as reported in Ref. [39]), however, do not give any evidence for such a maximum (see Fig. 4). The simulations indicate the same trend as that observed by Anselme *et al.* In this context, it is interesting to note that Mooij *et al.* [20] and Sheng *et al.* [41] used Monte Carlo simulations to study the vapor-liquid curve of a polymeric bead-spring model for various chain lengths. These studies also show a decrease of the critical density as a function of chain length. Such a decrease of the critical density with chain length is a general feature of long chain molecules, as was already pointed out by Flory.

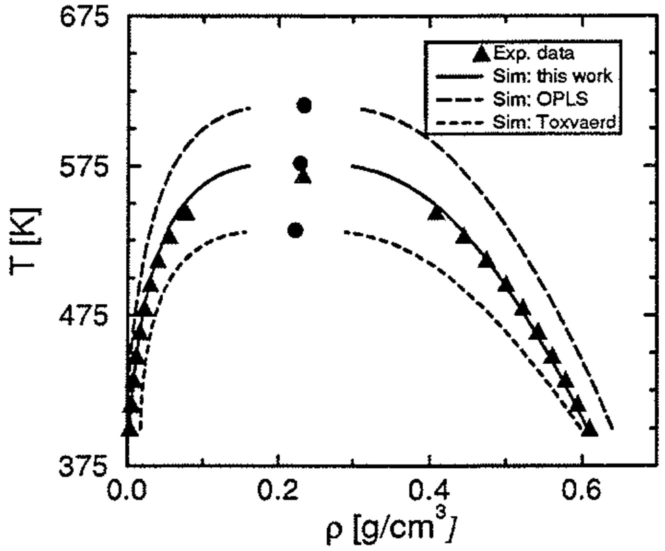

Fig. 3. Vapor-liquid curve of octane: comparison of Gibbs-ensemble simulations using the OPLS model of Jorgensen and co-workers [37], the model of Toxvaerd [38], and the model of Siepmann *et al.* [22, 36].

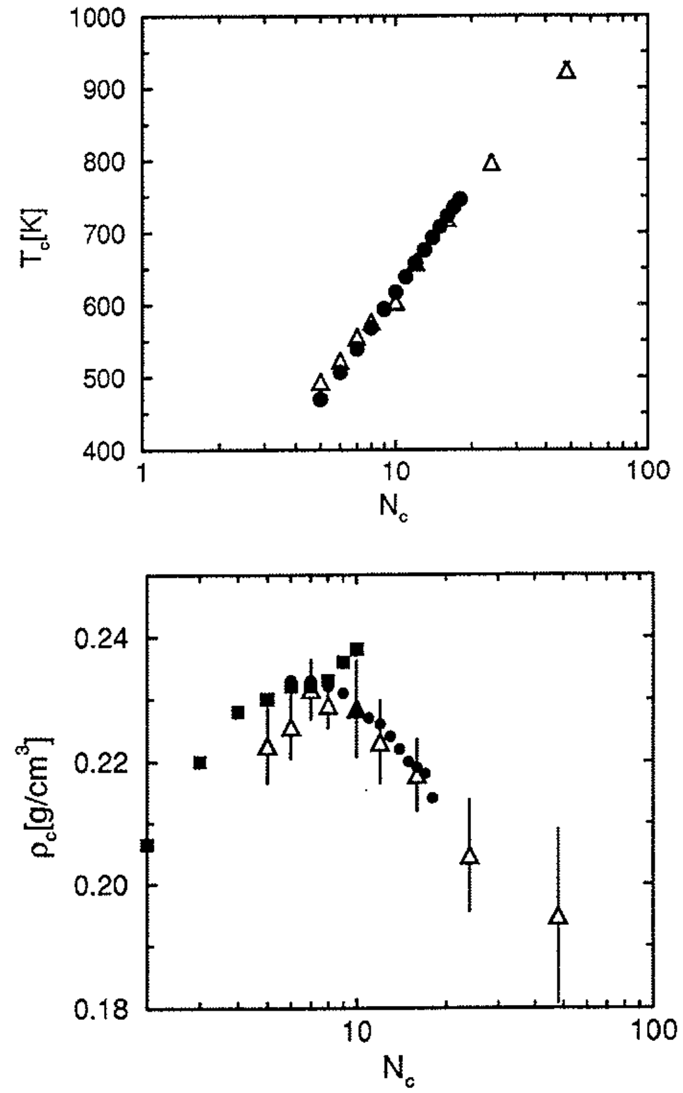

Fig. 4. Critical temperature T_c (top figure) and density ρ_c (bottom figure) as a function of carbon number N_c. The open symbols are the simulation data and the closed symbols are experimental data.

3.3. *Beyond chain molecules*

Thus far, the configurational-bias scheme has been presented exclusively as a method to generate conformations of chain molecules. In fact, the method is more general than that. It can be used as a scheme to perform collective rearrangements of any set of labeled coordinates. For example, the scheme can be used to carry out Monte Carlo moves to swap n small particles within a volume ΔV with one large particle that occupies the same (excluded) volume. This application of the CBMC scheme has been exploited by Biben [42] to study mixtures of large and small hard spheres. Gibbs-ensemble simulations of mixtures of spherical colloids and rod-like polymers were performed by Bolhuis [43] using CBMC-style particle swaps and a closely related approach was employed by Dijkstra to study phase separation in [44, 45] mixtures of large and small hard-core particles on a lattice. An application of CBMC to improve the sampling of ionic solutions has been proposed by Shelley and Patey [46].

A different application of the CBMC ideas is used by Esselink *et al.* [47] to develop an algorithm to perform Monte Carlo moves in parallel. Parallel Monte Carlo appears to be a contradiction in terms, since the Monte Carlo procedure is an intrinsically sequential process. One has to know whether the current move is accepted or rejected before one can continue with the next move. The conventional way of introducing parallelism is to distribute the energy calculation over various processors, or to farm out the calculation by performing separate simulations over various processors. Although the last algorithm is extremely efficient and requires minimum skills to use a parallel computer, it is not a truly parallel algorithm. For example, farming out a calculation is not very efficient if the equilibration of the system takes a significant amount of cpu time. In the algorithm of Esselink *et al.* several trial positions are generated in parallel and out of these trial positions the one with the highest probability of being accepted is selected with the highest probability. This selection step introduces a bias which is removed by adjusting the acceptance rules. The generation of each trial move, which includes the calculation of the energy (or Rosenbluth factor in the case of chain molecules), is distributed over the various processors. Loyens *et al.* have used this approach to perform phase equilibrium calculation in parallel using the Gibbs-ensemble technique [48].

4. Concluding remark

Industrial applications of molecular simulations to determine thermodynamic properties usually involve systems containing complex fluids. For these type of systems, in particular for systems containing long chain alkanes, the conventional simulation techniques are not sufficiently efficient. It is shown that the recently developed configurational-bias Monte Carlo technique is particularly suited to simulate the thermodynamic properties of these complex fluids.

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