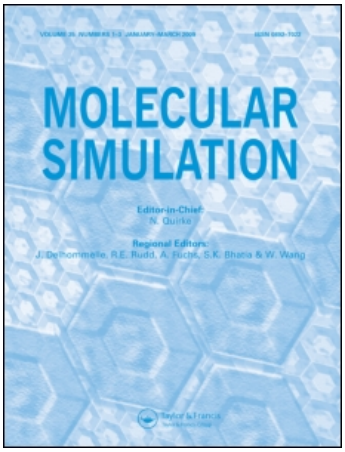

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ATOMISTIC MONTE CARLO SIMULATIONS OF LIQUIDS OF CHAIN MOLECULES CONFINED BY SOLID SURFACES: METHODS AND RECENT RESULTS

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The molecular arrangements of liquid tridecane near solid surfaces and in narrow slits have been studied by atomistic Monte Carlo computer simulations. A single surface perturbs the liquid over a distance of 1.5 nm, inducing the formation of progressively less dense and ordered layers of thickness 0.4 nm. Chains with atoms in the first layer tend to run parallel to the surface. The tendency to form layer structures is maintained or destroyed in narrow slits, depending on the slit thickness. For instance, it is slighly increased in slits of thickness 1.2 nm, while it is practically destroyed when the slit thickness is reduced to 1.0 nm. When added in small amounts, shorter-chain components are preferentially adsorbed at the solid surface, making the first layer of liquid in contact with these surfaces much less ordered.

KEY WORDS: Monte Carlo, chain molecules, solid surfaces

1 INTRODUCTION

The first application of the Monte Carlo method to the computer simulation of a liquid of chain molecules modelled at the atomic level (that is, with realistic chain structure, geometry and interatomic interactions), was published in 1980 [1]. The simulated system was a cubic cell of 3.04 nm edge filled with 31 straight-chain $C_{30}H_{62}$ molecules. As already usual with small molecule fluids, boundary effects were avoided considering this cell surrounded by a cubic array of identical cells. The chains were modelled as sequences of 30 point units with bond lengths and valence angles fixed at 0.154 nm and 112°, respectively, while the torsional angles were free to vary in the whole range $(0, 2\pi)$ with an appropriate torsional potential. A 6-exp potential function was used to model the interactions of non-bonded methylene units. The randomly generated initial guess was equilibrated at 400 K by using reptation movements with the algorithm of Metropolis *et al.* [2] (see later). The resuls of this study confirmed the belief of P. J. Flory [3] that the effects of long range intramolecular interactions are compensated in the isotropic bulk liquid by those of intermolecular interactions, such that the chain molecules assume their unperturbed conformational distribution.

The molecular shapes and arrangements of the chains are obviously perturbed when the environment is anisotropic, like in the multitude of different microphase organizations of amphiphilic molecules (i.e. monolayers, double layers, micelles) or in liquid

crystalline substances. A situation of this kind, that has been the subject of considerable experimental [4–9] and theoretical [10–18] work in the last few years, is that of a liquid of chain molecules near the surface of a solid. Understanding this situation is a key factor in the study of several important applications, such as adhesion, lubrication, composite materials etc. Atomistic computer models of straight-chain alkanes in broad slits with solid surfaces modelled as impenetrable walls [16], and in broad and narrow slits with atomistically structured surfaces [17–18] have been recently developed to study the molecular arrangements and the conformations of chain molecules near the surfaces. This paper reports on the simulation techniques in details and reviews the main results of these studies. New, unpublished data on mixtures of alkanes of different length are also reported.

2 MODELS AND METHODS

2.1 Chain molecules and force field

The straight-chain alkane molecules are modelled as unbranched sequences of N point units, with fixed bond lengths (0.153 nm) and fixed bond angles (112°). Units belonging to different chains or belonging to the same chain but separated by more than three skeletal bonds interact through a truncated 12-6 Lennard-Jones potential with minimum energy $-0.6\,\text{kJ mol}^{-1}$ at the distance of 0.4 nm. The truncation distance is taken to be 0.5 nm and the energy is shifted such to be zero at this distance. Furthermore, to speed up the calculations (see later), non-bonded distances smaller than 0.32 nm are forbidden, with the exception of those between units in the same chain separated by four bonds. The same 12-6 truncated potential is used for all the interactions of non-bonded units, including the interactions between the chain molecules and the units constituting the solid surfaces in [17,18]. The non-bonded interactions of units separated by three skeletal bonds in the same chain are separately computed by using a torsional potential of the form $V(\varphi) = (V_m/2)[x(1-\cos\varphi) + (1-x)(1-\cos 3\varphi)]$ with $V_m = 17\,\text{kJ mol}^{-1}$ and $x = 0.163$. This gives $2.1\,\text{kJ mol}^{-1}$ and $15\,\text{kJ mol}^{-1}$ for the energy difference and the barrier, respectively, between the trans ($\varphi = 0°$) and the gauche states of *n*-butane.

2.2 Model systems

The system modelled in calculations with impenetrable walls [16] (Model A) consists of an orthorombic cell with edges 15 nm in both the x and y directions and 5 nm in the z direction. The two faces perpendicular to the z axis are considered impenetrable, in the sense that they cannot be crossed by the C—C bonds, while periodic boundary conditions are imposed along the x and y directions (Fig. 1a). This cell has been filled with 2995 tridecane molecules and equilibrated at room temperature (300 K). Calculations for narrow slits of thickness comparable to the transverse diameter of the chain molecules have been performed in the model system of Figure 1b [17–18]. The system (Model B) consists of an orthorombic cell with edges 15 nm, 8 nm and 5 nm in the x, y and z directions, respectively. Periodic boundary conditions are imposed along all

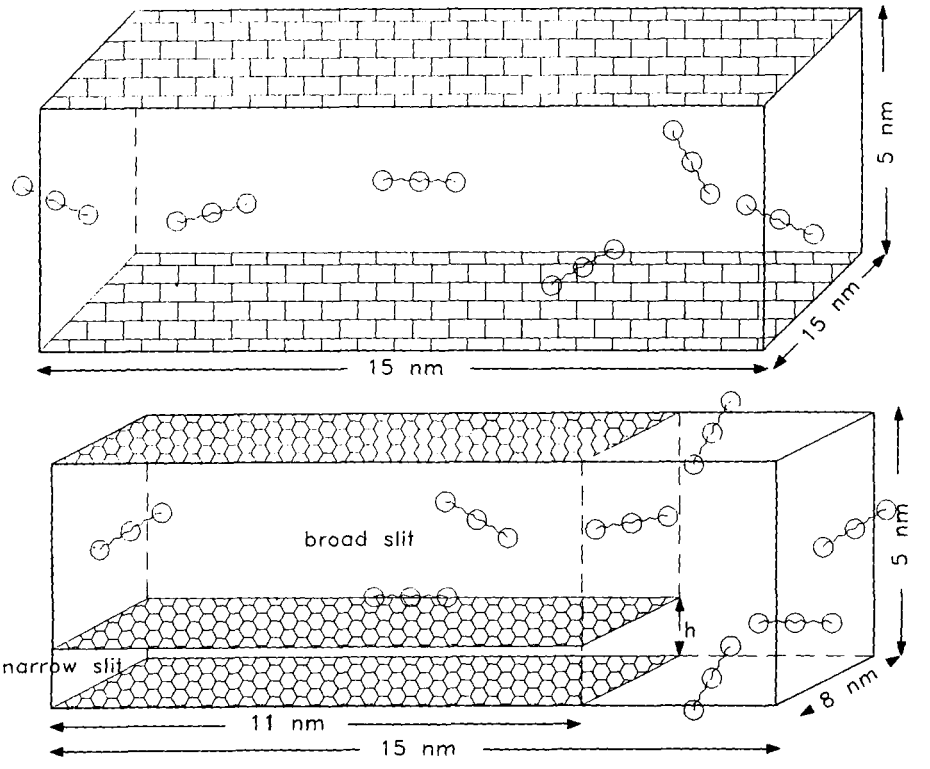

Figure 1 Schematic view of the basic orthorombic cells used in the simulations. **a** Model A, impenetrable walls; **b** Model B atomistic walls ($h = 1.2$ nm in the example shown).

three directions. The solid surfaces are modelled as planar arrays of hexagonally packed units perpendicular to the z axis. The surfaces are infinitely extended in the y direction, while they are extended only from $x = 0$ to $x = 11.0$ nm in the x direction. Two separate calculations have been performed, with solid surfaces placed at $z = 0$ and $z = 1.2$ nm in the first case (Model B12), and at $z = 0$ and $z = 1.0$ nm in the second case (Model B10). Due to the periodicity along the z axis, the region of the cell between $x = 0$ and $x = 11.0$ nm consists then of two slits of thickness 1.2 nm and 3.8 nm in Model B12, and of thickness 1.0 nm and 4.0 nm in Model B10. In both cases, the cell has been filled with 1297 molecules of tridecane. It is assumed that the properties of molecules located between $x = 2.0$ nm and $x = 9.0$ nm are not influenced by border effects and are practically coincident with those of molecules between solid surfaces infinitely extended in both the x and y directions. Model B has been also used for calculations on mixtures of alkanes of different length. In a first calculation [18], both models B12 and B10 have been equilibrated with 1190 molecules of tridecane and 819 molecules of a diluent having the size and interactions of a methylene group (Models B12d and B10d, respectively). In the new calculations reported in this paper, model B12 has been filled with 1141 molecules of tridecane and 330 molecules of pentane (Model B12p).

2.3 *Initialization*

Since the reptation method used in the subsequent equilibration is highly efficient for the short chains modelled in this work, the details of the initializiation are not crucial for the success of the simulation. However, it is obviously useful to have a starting point not too high in energy, with particular reference to the interactions of non-bonded groups. For this reason, the systems have been initialized treating all the units (including those of the solid surfaces in models of the B type) as rigid spheres with 0.32 nm diameter, which gives a radial distribution function not too far from that at the equilibrium. The general procedure used in the initialization is the following. Suppose k molecules have been already placed in the cell. The location of the first unit of molecule $k+1$ is selected at random and tested for the rigid sphere condition. The location of the second unit is selected at random on a spherical surface of radius equal to the C—C bond length, centered on the first unit. It is then tested for the rigid sphere condition and, in the case of Model A, also for the condition that bond C_1—C_2 does not cross the impenetrable walls. After a number N_a of attempts, the first unit is deleted and the chain is restarted in a new position. When the first j units ($j > 1$) of the molecule have been already placed, the location of unit $j+1$ is selected at random on the proper circle such that the angle C_{j-1}—C_j—C_{j+1} is the fixed C—C—C bond angle. The location of unit $j+1$ is then tested for the appropriate conditions (rigid sphere condition and, in the case of Model A, impenetrability of the walls). After N_a failures, the current location of unit j is deleted and the procedure restarted from unit j when $j > 3$. When $j \leqslant 3$, the whole chain is deleted and restarted from the first unit in a new random location. This also happens when the total number of attempts for the growing $k+1$ chain becomes greater than a limiting value, N_t. The values used for N_t and N_a are only dictated by convenience. The initialization of the systems discussed in this paper, which has been performed with $N_a = 20$ and with $N_t = 1000$, is quite fast. For instance, model B10 is initialized in less than 100s on a IBM RISC/6000 mod. 550. The timing data reported in the following are always referred to this machine.

2.4 *Equilibration*

All the model systems have been studied at room temperature (300 K). The starting situations, which are obviously of high energy, have been equilibrated by standard Monte Carlo techniques using reptation moves for the chain molecules and local displacements for the diluent molecules, when present (Models B12d and B10d). At each step, a unit is selected at random. When this unit is a diluent molecule, new trial coordinates are generated inside a sphere of 0.2 nm diameter centered on the old position. When the selected unit belongs to a chain molecule, one of the two terminal units of the chain is removed and a new unit is randomly added at the opposite chain end. In all cases, the new situation is a accepted or rejected according to the outcome of a Boltzmann test as suggested by Metropolis and coll[2]. (i.e., it is accepted when a random number in the [0, 1] range is less then $\exp(-\Delta E/RT)$, with ΔE the total energy difference between the new and the old situation; otherwise, the old situation is restored and a new attempt is started). The equilibration is followed by monitoring the behavior of all the relevant properties of the system under study. In the case of Model

B12p, taken as an example, all the properties reported in the next section reach stationary values after 3×10^7 attempts, corresponding to 2×10^6 accepted moves. This number of attempted moves requires 8 hours of CPU and is defined as a cycle. The equilibration has been continued for 9 more cycles, to the sure that any trace of the starting point was lost. 10 equilibrium situations have been then collected at intervals of two cycles, and used to evaluate the various properties discussed in the next section. Table 1 shows the coordinates of the central unit of the tridecane chains numbered 1 and 2 and of the pentane chains numbered 1 and 2 in Model B12p (no attemps were made to select the most mobile molecules) at the completion of five to these cycles. Note that the three central lines correspond to consecutive equilibrium situations in the final set. The mobility is seen to be large enough to ensure that the 10 situations collected are descriptive of the equilibrium state of the model system.

The assumption that the molecular arrangements obtained after prolonged equilibration correspond to a state of thermal equilibrium can be tested as in Ref. 16. In this case, the content of the basic cell was perturbed by introducing an arbitrary attraction between the impenetrable walls and the chain ends. As a result, three times more chain ends moved to the walls. When the additional attraction was removed, however, the original arrangements of the chains were rapidly restored, thus supporting the assumption that these arrangements are representative of the equilibrium state.

2.5 *Evaluation of non-bonded interactions*

The slowest step in Monte Carlo calculations on dense atomistic systems like those studied in this work is obviously the evaluation of the non-bonded interactions. For instance, each reptation attempt requires that the non-bonded interaction energy with the rest of the system be calculated for both the unit to be removed from the selected chain end and the trail unit to be added at the opposite end. To calculate each one of these energies, the distance from the given unit to all the non-bonded units in the basic cell or to their images in the adjacent cells are needed. Since all the simulated systems contain more than 15000 total units, the attainment of an equilibrium would be practically impossible, unless methods are applied to speed up this step. The approximation that the Lennard-Jones potential is truncated and shifted such that the interaction energy be zero at the truncation distance is crucial in this respect. In fact, it

Table 1 Coordinates (in nm) of the central units of two tridecane chains and of two pentane chains in Model B12p at the completion of various calculation cycles.

	Tridecane 1			*Tridecane 2*			*Pentane 1*			*Pentane 2*		
Cycle No.	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
10	9.7	5.6	3.9	11.2	7.3	2.8	4.0	7.5	2.2	5.8	1.8	0.8
16	8.6	6.3	4.3	13.4	7.6	1.6	3.6	8.0	1.5	4.4	1.9	0.7
18	7.2	7.9	4.3	12.9	7.1	1.8	1.8	5.5	1.6	2.9	2.1	0.4
20	6.9	7.7	4.3	14.6	7.2	0.3	2.7	6.1	1.6	3.9	3.3	0.7
28	8.2	7.0	4.0	0.0	7.0	4.7	2.9	6.7	2.8	3.0	4.2	0.8

implies that the total non-bonded energy of a unit with coordinates **P** in the basic cell can be evaluated considering only those units which are at a distance from **P** smaller than the truncation distance. Of course, when **P** is close to the cell surfaces, the periodicity of the system has to be taken into account. This calculation can be made quite fast by use of a well known device. The basic cell is considered to be a orthorombic array of boxes with edges not smaller than the truncation distance, and a list is made of the units contained in each box. Whenever a unit changes position, the list is changed accordingly. Although it may be convenient to have cubic boxes, with edges exactly equal to the truncation distance, it has not to be necessarily so. The non-bonded interaction energy of a unit in **P** can be then evaluated considering only the units contained in the same box of **P** and in the 26 immediately adjacent boxes (taking into account the periodicity). This makes the calculation of the energy much faster, and independent from the overall size of the system. The calculation is even faster when the units are treated as rigid spheres (see the Initialization), since in this case the trial position can be rejected as soon as a distance from a preexisting unit is found to be smaller than the rigid sphere diameter. For this reason, the calculation of the non-bonded energies is always performed in two steps. In the first step, a table is prepared of the square distances from **P** of all the non-bonded units at a distance smaller than the truncation distance. In the second step, the table is used to calculate the value of the non-bonded energy. When attempting a move, it is convenient to evaluate the non-bonded energy of the trial situation first, such that this situation can be rejected directly in the first step when a distance is found smaller than the preselected 0.32 nm rigid sphere diameter (see before).

3 RESULTS AND DISCUSSION

The simulations performed in Refs. 16 and 17 for pure liquid tridecane indicate that the presence of a solid surface perturbs the liquid over a distance of approximately 1.5 nm. In fact, all the properties of tridecane chains with center of mass at distances from the nearest solid surface greater than 1.5 nm are practically coincident with those of ideal unperturbed RIS chains. Hence, the molecular arrangements near the surfaces in slits of thickness greater than 3.0 nm are representative of those near a single surface in equilibrium with the bulk liquid. The results obtained for impenetrable walls [16] and for atomistically structured surfaces [17] are substantially similar. As far as the distribution of units is concerned, the perturbation consists in a series of progressively less intense maxima and minima of the density, with a periodicity of approximately 0.4 nm. The first, most intense maximum is located at 0.13 nm from the surface when the latter is simulated as an impenetrable wall, while it is located at 0.4 nm from atomistically structured surfaces. In other words, an impenetrable wall mimicks the presence of a structured surface shifted 0.27 nm further on.

When the slit thickness is comparable to the transverse diameter of the chain molecules, the behavior of the density is markedly dependent on the separation of the two surfaces. Figure 2 shows, as an example, the distribution of C atoms in the broad and in the narrow slit for Model B12p, containing a mixture of pentane and tridecane. The density maxima of the tridecane C atoms in the narrow slit are seen to be slightly

more intense, and the intermediate minimum slightly deeper, than the first maximum and minimum observed in the broad slit. This is in full agreement with the results of the study of Models B12 and B12d, showing that in a slit of thickness 1.2 nm the tendency of the chain molecules to form densely packed layers of methyl and methylene units near the solid surfaces is slightly increased with respect to that near a single solid surface. On the contrary, the results obtained with Models B10 and B10d indicate that this tendency is almost totally destroyed when the slit thickness is reduced to 1.0 nm, since the two maxima are in this case much less intense than in broad slits and the intermediate minimum is practically absent.

The peculiar setup of all models of type B (see Fig. 1b) is such that the liquid in the narrow slits is in equilibrium with the bulk unperturbed liquid at room temperature and atmospheric pressure [17]. This gives rise to a quite interesting behavior of the total density in the two narrow slits. In fact, the total number of units in the 1.2 nm slit is found to be approximately twice the number in a layer of 0.6 nm thickness near a single solid surface, while the number of units in the 1.0 nm slits is 10% less than twice the corresponding number in a layer of thickness 0.5 nm near a single surface. In other words, the tridecane molecules tend to avoid the slit of thickness 1.0 nm, in agreement with the simple observation that two layers of units can be accommodated quite well in a slit of thickness 1.2 nm, but not in a slit of thickness 1.0 nm.

A second point of interest concerns the arrangements of the chain molecules near a single solid surface and in narrow slits. In order to characterize these arrangements, the chains having at least one methyl end in a layer of thickness 0.5 nm or 0.6 nm near

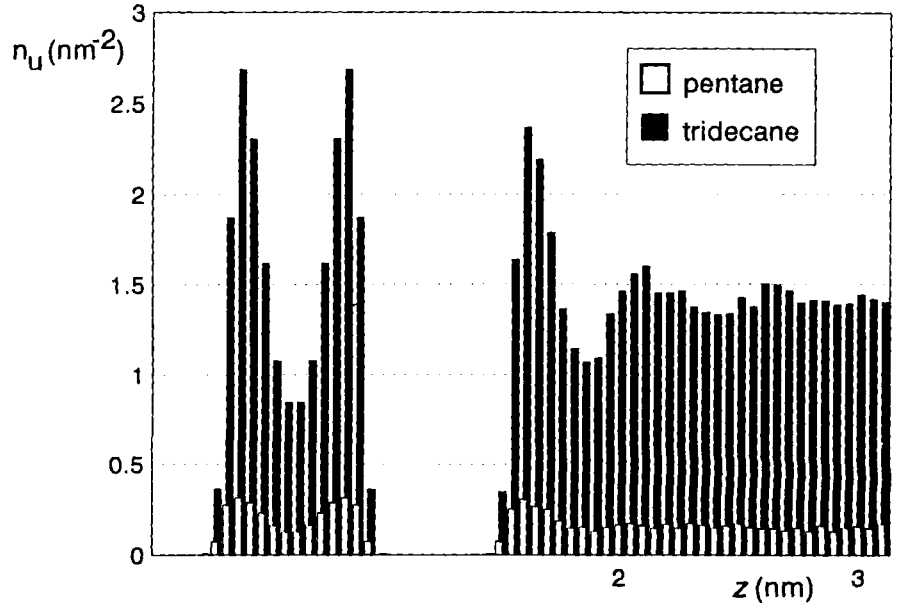

Figure 2 The distribution of C atoms belonging to pentane and tridecane molecules between the solid surfaces ($2.0 < x < 9.0$ nm) in Model B12p. n_u is the number of C atoms per square nanometer in sublayers of thickness 0.05 nm parallel to the xy plane at the given value of z.

the surfaces have been classified as: chains having all the units in the same layer (layer chains), chains having the two methyl ends in the same layer and at least one unit outside (loop chains), and chains having the other methyl end outside the given layer (bridge chains in narrow slit, tie chains in broad slits). The fractions (in percent) of the various types of chains are shown in Table 2. For each entry, the first number refers to Models B12 and B10, the second number to Models B12d and B10d and the third number to Model B12p. As far as the pure liquid is concerned, Table 2 confirms that the tendency to form molecular layers near the surfaces is increased in a narrow slit of thickness 1.2 nm with respect to broad slits, while this tendency is destroyed in a slit of thickness 1.0 nm. For instance, 12% of the chains having a methyl end in layer of thickness 0.5 nm near the surfaces of the broad slits are layer chains. This figure is doubled (25%) in a similar layer in the 1.2 nm slit, while it is only 5% when the slit thickness is reduced to 1.0 nm. The latter effect is associated with a large increase of the fraction of loop chains, going from 26% in broad slits to 49% in the 1.0 nm slit. Table 2 also shows that the molecular arrangements near the surfaces are strongly influenced by the presence of the small amounts of a short-chain component. In spite of the different composition of the two systems, the data obtained for Model B12d in Ref. 18 and for Model B12p in the present work are practically coincident. In particular, the fractions of layer and loop chains in a layer of thickness 0.5 nm near the surfaces are much smaller than in the case of the pure liquid, while the fraction of bridge/tie chains is correspondingly increased. In other words, adding a short-chain component to a liquid of chain molecules makes the liquid in contact with the surfaces much less ordered.

A third interesting result concerns the selective adsorption at the solid surfaces of chain molecules of different length. All the calculations performed up to now on pure liquids, including those in which the chain molecules have been modelled as idealized necklaces of beads [12, 14], indicate that the chain ends are preferentially adsorbed at the surfaces. For instance, nearly 50% of all the units in the first 0.05 nm near the impenetrable walls in Model A are methyl groups or methylene units bonded to methyl groups [16]. Similar results have been obtained in Ref. 17 for models B10 and B12. This effect originates from the higher restrictions imposed by the surface on the orientational and conformational freedom of the internal chain segments with respect to those

Table 2 The fraction (in percent) of all the tridecane chains having at least one methyl group in a layer of the indicated thickness near the solid surfaces and having: all the units in the same layer (layer chains); the other methyl group in the same layer and at least one unit outside (loop chains); the other methyl group outside the given layer (bridge/tie chains). For each entry, the first number refers to Model B12 or B10, the second number to Model B12d or B10d and the third number to Model B12p.

	1.2 nm slit		*1.0 nm slit*	*Single plate*	
	0.6 nm layer	*0.5 nm layer*	*0.5 nm layer*	*0.6 nm layer*	*0.5 nm layer*
Layer chains	42–28	25–14–16	5–4	33–20	12–8–8
Loop chains	9–8	20–14–14	49–32	12–8	26–13–14
Bridge/tie chains	49–64	55–72–70	46–64	55–72	62–79–78

of the terminal segments. Not unexpectedly, this same effect influences the composition near the solid surfaces of mixtures of tridecane with shorter chains. Figure 3 shows the fraction of pentane carbon atoms (f_p, that is the number of C atoms belonging to pentane molecules divided by the total number of C atoms) in sublayers of 0.05 nm thickness in Model B12p as a function of the position of the sublayer along the z axis. The average value of f_p in the whole system is 0.1. The behavior of f_p in the narrow slit is practically identical to that in the first 0.6 nm near the surfaces in the broad slit. In particular, f_p is always higher than 0.1 in these regions (note that value $f_p = 0.25$ observed in the first sublayer near the surfaces in scarcely significant, since this sublayer is practically empty; see Fig. 2). In practice, 12% of the C atoms in the first 0.6 nm near a surface belong to pentane molecules, indicating that the shorter molecules are preferentially adsorbed at the surfaces both in broad and in narrow slits. As expected, the tendency to a preferential adsorption of the shorter component increases with increasing the chain length difference of the two components. For instance, the overall fraction of diluent in Models B12d and B10d is 0.05. After equilibration, the fraction of diluent in the bulk has been found to be only 0.045, while near the surfaces it is as high as 0.10, that is more than twice the bulk value [18]. Note that the shorter components are not more ordered than the tridecane chains (see, for instance, Fig. 2), while pure liquids of short chains show more pronounced layering near surfaces, with density modulations that are more extended into the liquid than in the case of longer chains [19]. This is due to the fact that the concentration of shorter components at the surfaces is anyway small in the two cases considered, such that these molecules are mainly surrounded by

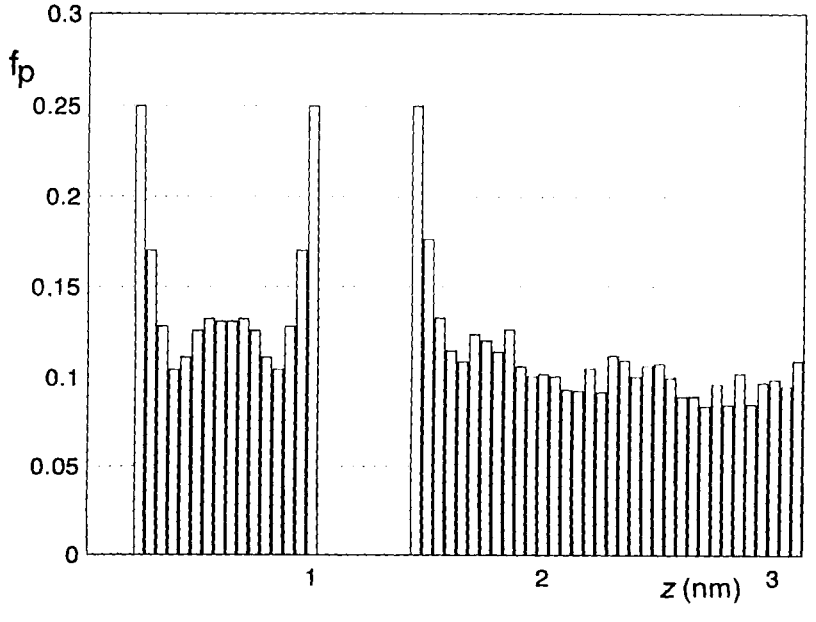

Figure 3 The fraction, f_p, of C atoms belonging to pentane molecules in sublayers of thickness 0.05 nm parallel to the xy plane in Model B12p as a function of z.

disordered tridecane chains, rather than by well packed, identical molecules as in the pure liquid.

4 CONCLUSIONS

The main conclusions of the Monte Carlo simulation studies discussed in this paper can be summarized as follows:

(i) a single solid surface perturbs the liquid over a distance of approximately 1.5 nm; the perturbation consists of layers with thickness approximately equal to 0.4 nm, progressively less well packed with increasing the distance from the surface; chains with units in the first of these layers tend to run parallel to the surface;

(ii) the molecular arrangements in narrow slits with thickness comparable to the transverse diameter of the chains depend strongly on the slit thickness; in particular, the tendency to form layer structures is increased in slits of thickness 1.2 nm, while it is destroyed in slits of thickness 1.0 nm;

(iii) short-chain components tend to concentrate in narrow slits and near single solid surfaces; even small amounts of these components make the liquid in contact with the surfaces much less ordered.

The results of the simulations are in very good agreement with experiments. For instance, the force between two smooth mica surfaces immersed in liquid alkanes shows an oscillatory behavior when the distance of the surfaces is shorter than 3 nm [18]. The experimental observation that the periodicity is independent on the chain length and approximately equal to 0.4 nm supports the conclusion that the chain molecules tend to form near the surfaces dense and ordered layers of thickness comparable to the transverse molecular diameter [8]. The same conclusion is also suggested by the surprising increase of the apparent dynamic shear viscosity found for hexadecane films when the thickness is reduced to 0.8 nm [7]. In agreement with the simulations, the two-dimensional order in the surfacial alkane layers is only partial, as shown by the fact that sliding the surfaces leads to a more ordered state of these layers [9]. The latter experiments also indicate that the surfacial order is strongly reduced by the presence of small amounts of water, methanol and other short-chain components [9].

The good qualitative agreement between calculated properties and experiments confirms that computer models obtained using the simulation techniques discussed in this peper represent, in spite of their intrinsically approximate nature, a good description of the molecular arrangements in systems of chain molecules. This is true not only for the unperturbed bulk liquid, but also in complex environments in which these arrangements are perturbed by the presence of strong directional constraints. Models of this kind are able to explain the general aspects of the experimentally observed behaviors, and may reveal unsuspectedly important new features. For instance, the finding that the composition of the first layer of units in constant with a surface tends to be largely different from that the bulk – both in pure liquids and in mixtures with short-chain components – is obviously of outmost importance for the theoretical treatment of the interactions of systems of chain molecules with a solid. The application

of analogous techniques to other interesting situations, like for instance the interface between two immiscible polymers, is currently under way in this laboratory.

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