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The effect of branching on the structure of confined thin films of alkanes

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Abstract. – We report computer simulations in the grand canonical ensemble of a system of several linear and branched alkanes between two solid surfaces. We computed the solvation force exerted by the fluid on the plates. The solvation force for linear decane oscillates with distance with a periodicity close to the width of the molecules. The branched alkanes (2-methylundecane and 2-methylheptane) show a similar oscillatory behaviour; however, the oscillations are decreased and are shifted to the attractive regime.

Introduction. – The behaviour of fluids in contact with solid surfaces or confined in microscopic pores is of fundamental as well as practical importance. They play an important role in applications as engine lubrication, zeolites, clay swell or in the stability of colloidal systems, like emulsions, paints, surface coatings, etc. The molecular structure of the confined fluid can differ dramatically from that in the bulk. It is therefore that we cannot use our knowledge of bulk fluids, when we are dealing with fluids in confined geometries. Due to its technological importance, significant experimental and theoretical effort has been dedicated to this subject [1].

Historically, the DLVO theory (Derjaguin-Landau-Verwey-Overbeek) and the Van der Waals theory have been used to describe colloidal stability in bulk systems. However, if two particles or surfaces approach each other closer than a few molecular diameters, these theories have been found to be inadequate to predict the interactions between the surfaces, since other forces become important [2]. These short-range forces are called solvation forces, or hydration forces in the case of water.

Experimentally, the surface force apparatus can be used to measure very accurately the forces acting on two solid surfaces immersed in a fluid. These short-range solvation forces were found to be monotonically repulsive, monotonically attractive or oscillatory with distance. The oscillatory behaviour of the solvation force is now well understood for simple spherical molecules.

Theoretical work and computer simulations of Lennard-Jones fluids and hard spheres show that the oscillatory solvation force originates from the ordering of the molecules in layers when the fluid is confined by the surfaces [2]. The solvation forces depend strongly on the chemical and physical nature of the surfaces, for example, whether they are hydrophilic,

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(*) Present address: H. H. Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, UK hydrophobic, smooth, corrugated, etc. On the other hand, the oscillatory behaviour is very sensitive for the detailed chemical structure of the molecules and the ability of the molecules to order. One of the most striking examples of this sensitivity is the difference between the solvation force of linear and branched alkanes. For example, experiments showed that a single methyl side group on a linear octadecane chain can completely eliminate the oscillations in the solvation force [3], [4]. This phenomenon may explain why branched alkanes are better lubricants than linear ones. A similar difference was observed in force measurements of low-molecular-weight polymer melts. Unbranched polydimethylsiloxane (PDMS) exhibits a short-range oscillatory solvation force profile, while branched polybutadiene (PB) shows only a monotonically repulsive solvation force [5]. However, recent computer simulations of octane and branched iso-octane did not reveal this unexpected difference in the solvation force profiles, casting doubts on the experiments [6]. Also recent experiments of 3-methylundecane show that the solvation force still shows an oscillatory behaviour; however, the amplitudes of the oscillations are three times smaller than for linear undecane [7]. In this article, we show by computer simulation that there is a difference in the solvation force for branched and unbranched alkanes. Our results show an oscillatory behaviour for the solvation force of linear decane with a periodicity close to the width of the alkanes. For 2-methylundecane and 2-methylheptane, we still found oscillations in the solvation force, but the amplitudes of the oscillations are decreased with respect to n-decane. The solvation force, however, is shifted to the attractive region.

Monte Carlo calculations. – The surface force apparatus measures the force between two molecularly smooth mica surfaces immersed in a fluid as a function of the distance. Thus the confined fluid between the surfaces is in equilibrium with the bulk fluid outside the plates. This apparatus can, hence, be considered as a system with two plates with an area A held at a distance H apart in a fluid with a chemical potential μ. At small plate separation, the structure of the confined fluid differs substantially from that of the bulk, and hence a net force is exerted perpendicular to the plates. This solvation force can be measured by the surface force apparatus.

In order to compute the solvation force correctly, we have to perform simulations for different plate separations at a fixed chemical potential. We, therefore, performed grand-canonical Monte Carlo (GCMC) simulations of alkanes between two plates, where the independent variables are the chemical potential μ, the volume $V = AH$ and the temperature T.

Conventional Monte Carlo schemes are not sufficiently efficient to ensure rapid equilibration, as direct insertion of a flexible particle in a dense fluid almost always results in an overlap with one of the other chains in the fluid. For a faster equilibration of the alkanes, it is essential to use the configurational bias Monte Carlo (CBMC) method. In the CBMC method, the construction of the alkane conformations proceeds atom by atom. To add an atom to the chain, we generate a fixed number of trial atoms in such a way that the probability of finding a given trial atom is given by the Boltzmann weight corresponding to the internal energy, *i.e.* the sum of the bond-bending potential and the torsion potential. We then choose one of the trial segments with a probability proportional to the external energy, *i.e.* the non-bonded interactions. This algorithm biases the insertion of chains in such a way that chains with favourable internal energies are inserted in regions with favourable external energies. Overlap with other chains is in this way avoided. For more technical details on the implementation of the CBMC method, we refer the reader to ref. [8], [9].

Most runs consisted of at least 10^8 cycles. In each cycle, an attempt is made to regrow a part of the polymer using the CBMC method and a removal or insertion of a particle in the box is attempted. On average, once every two cycles, a random displacement and random

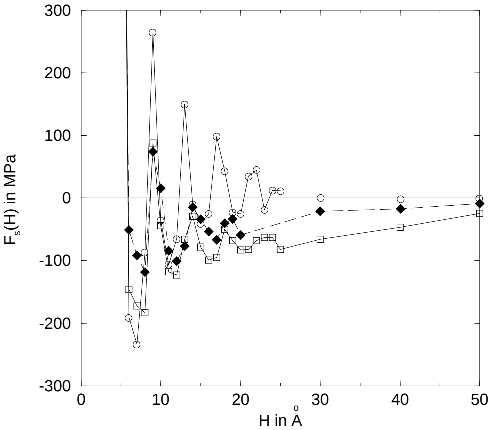

Fig. 1. – The solvation force F_s *vs.* the distance H of the solid plates in Å for a system of n-decane (open circles), 2-methylheptane (solid diamonds), and 2-methylundecane (open squares).

rotation of a particle in the box is attempted and once every five cycles, a whole polymer is regrown at a random place in the box using the CBMC method.

The alkanes are modeled by the united atom approximation, where every CH_3 or CH_2 group is described as a single interaction site. The non-bonded dispersive interactions between these "united atoms" of different molecules or within a molecule (when two atoms are more than four atoms apart) are described with a Lennard-Jones potential. The potential parameters for unlike-bead interactions are calculated using the Lorentz-Berthelot rules. We used fixed bond lengths and a harmonic bond angle bending. Changes in the dihedral angle are described by a torsion potential. The potentials for the linear alkanes are the same as in the model of Smit *et al.*, which were derived from calculations of the vapour-liquid phase equilibria of n-alkanes [9]. For the branched alkanes, we used the model of Wang *et al.*, which is based on Jorgensen's optimized potentials for liquid simulations (OPLS) [6].

In our model, we confined the alkane fluid in the z-direction by two flat surfaces. However, experimentally, the force is measured between curved surfaces, but using the Derjaguin approximation the free energy per unit area of curved surfaces can be related to a force between flat surfaces [2]. In the vicinity of the surfaces, the alkanes experience a potential field due to the solid surfaces. In our simulations, we used a 9-3 wall potential.

Results. – GCMC simulations were performed on a system of decane, 2-methylheptane and 2-methylundecane. The fluid is confined in the z-direction by two solid surfaces of 34 × 34 Å. The plate separations vary from about 5 to 50 Å. In the x- and y-direction, we used periodic boundary conditions, such that an infinite, periodic system is simulated. In all the simulations the temperature T is fixed at a value of 298 K and the chemical potential is such that the density of the reservoir is 0.717 ± 0.008 g/cm^3 for all species, which corresponds to a liquid phase. In our simulations, we measured the solvation force

$$F_\mathrm{s}(H) = \left\langle -\frac{1}{2A}\left[\sum_{i=1}^{N} \frac{\partial V_\mathrm{s}(z_i)}{\partial z_i} - \frac{\partial V_\mathrm{s}(H-z_i)}{\partial z_i}\right]\right\rangle , \qquad (1)$$

where $V_\mathrm{s}(z)$ is the 9-3 wall potential, N the number of particles and the brackets $\langle \cdots \rangle$ denotes the ensemble average $\langle \cdots \rangle_{\mu,T,H}$. By symmetry, we find that the magnitude of the force on the upper surface is equal to that on the lower surface. In fig. 1 we plot the solvation force *vs.* the distance H between the plates for n-decane, 2-methylheptane and 2-methylundecane. For n-decane, we observe strong oscillations around zero with a periodicity of 4-4.5 Å. However, in

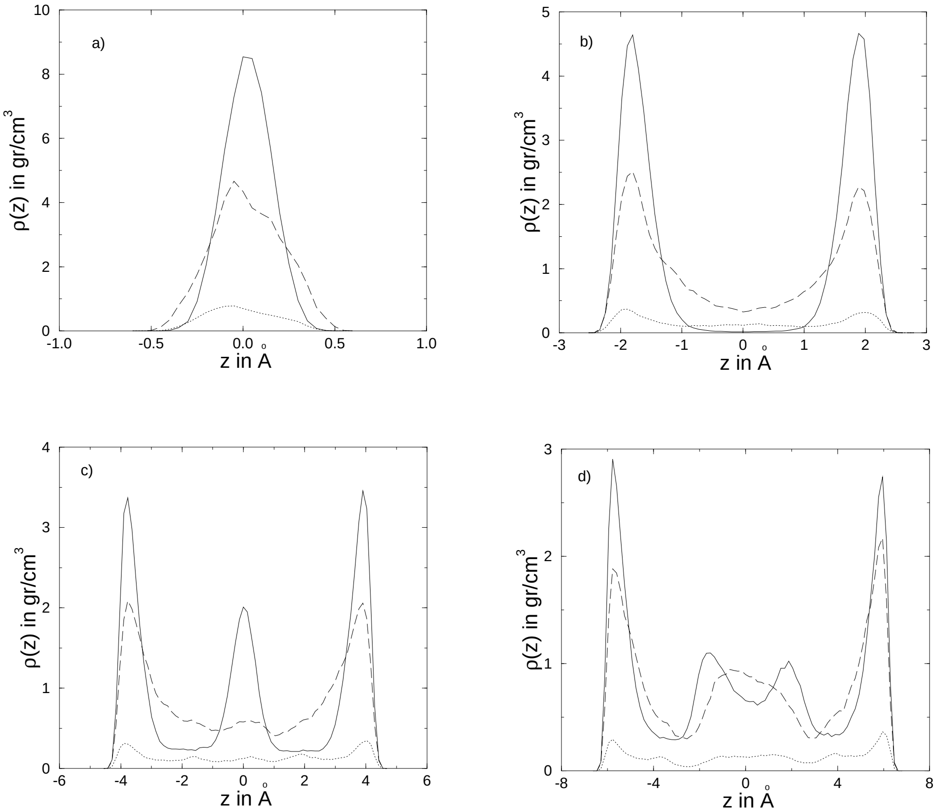

Fig. 2. – Density profiles $\rho(z)$ *vs.* z in Å at different plate separations: *a*) 5 Å, *b*) 9 Å, *c*) 13 Å, and *d*) 17 Å for n-decane (solid line) and 2-methylundecane for all atoms (dashed line) and for only the branched methylgroups (dotted line).

the case of 2-methylheptane and 2-methylundecane, the oscillations are less pronounced and are shifted to the attractive region. At large plate separations, the solvation force for the branched alkanes goes to zero. For 2-methylheptane the solvation force is zero at plate separations larger than 30 Å. For 2-methylundecane, we find that the solvation force goes to zero slowly with increasing plate separation. In fig. 2, we plot $\rho(z)$, the mass density distribution for several values of H. The results for n-decane are in good agreement with those in ref. [10], [11]. For a plate separation of 5 Å, we find one layer between the plates. For a separation of 9, 13, and 17 Å, two, three and four layers are formed, respectively. In fig. 2, we also plot the density profiles of 2-methylundecane and that of the branched methylgroups. We observe that the profiles of decane are more strongly peaked than those of 2-methylundecane. We also see from the density profiles for only the branched methylgroups that one branched group is in the fluid layer, while the other lies between the fluid layers. In fig. 3, we show a typical configuration of a layer of n-decane at $H = 5$ Å. The density of this film is close to the bulk liquid density of n-decane and the alkanes are disordered in position and orientation. We, therefore, conclude that the configuration is fluid-like. In fig. 4, typical snapshots are shown of n-decanes and 2-methylundecanes adsorbed in a slit with a slitwidth of 9 Å and 13 Å, respectively. We see clearly that discrete fluid layers are formed in the case of n-decanes, while the fluid is more homogeneous in the case of 2-methylundecane.

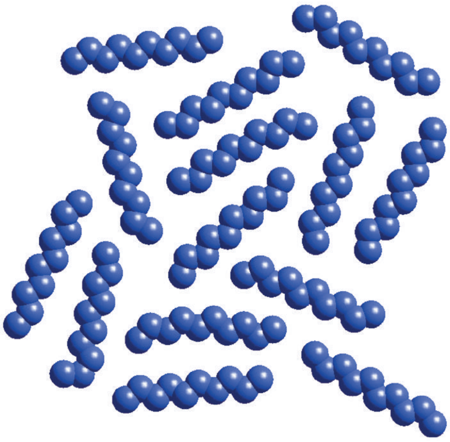

Fig. 3. – A typical configuration of the disordered fluid layer (top view) of n-decane formed between the plates. The two plates are in the same plane as the picture.

Discussion. – If we compare our results with the experimental data of ref. [3], [7], we observe two remarkable features. First of all, we still find oscillations in the solvation force of branched alkanes. From fig. 2, 3, and 4, we can conclude that the origin of oscillations in the solvation force lies in the ordering of the molecules in fluid layers. In the case of n-decane, well-defined fluid layers are formed. However, the ability of branched alkanes to form discrete layers is reduced due to simple packing arguments, but is not completely eliminated, as can be seen in fig. 2. This explains the two or three times weaker oscillations in our results in the case of branched alkanes, which agree well with the factor of three found in Granick's experiments of 3-methylundecane and linear undecane. In the experiments of Israelachvili *et al.*, no oscillations are found in the solvation force. However, their results show that the solvation force could not be measured accurately and a degree of scatter is found in their data of the same order as the amplitudes of the oscillations in Granick's data. The other surprising feature in our results is that the solvation force of branched alkanes is shifted to the attractive region. From the density profiles of fig. 2, we can understand why the branched alkanes exhibit a predominantly attractive force between the plates. The reason is that repulsive contributions to the solvation force stem only from particles close to the wall, *i.e.* $-\partial V_\mathrm{s}(z)/\partial z > 0$ when $z < 2.6395$ Å. Thus, a repulsive solvation force can only be obtained when there is a strong ordering of molecules close to the wall. Figure 2 shows that in the case of branched alkanes, the ordering

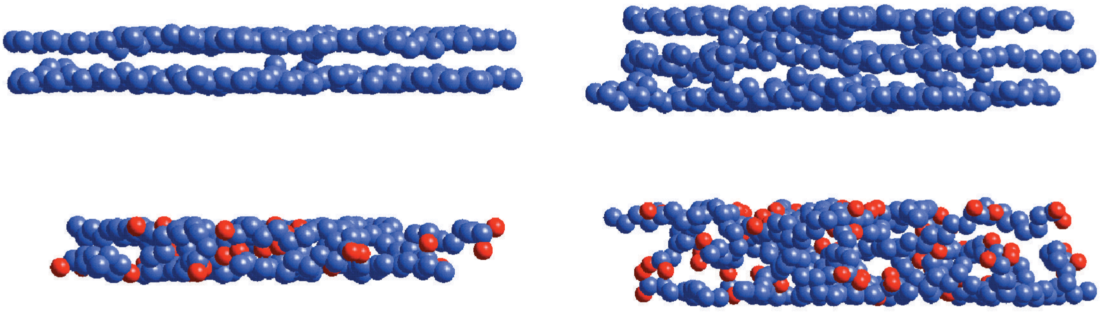

Fig. 4. – A typical snapshot (side view) of n-decane (top) and 2-methylundecane (bottom) confined between two solid plates at a plate separation of 9 Å (left) and 13 Å (right). The branched methyl-groups are red. The two plates are perpendicular to the picture.

of the molecules close to the wall is smaller in comparison with n-decanes. This is the reason why an attractive solvation force is obtained for branched alkanes. This attractive solvation force agrees with the experiments of Israelachvili *et al.* They observed a long-range attractive force at least till a plate separation of 30 Å. The branched methylgroups frustrate the packing in one layer and the amount of interdigitation increases. Interdigitation describes to what extent individual molecules belong to a specific layer. This feature that more side branches (like squalane) give more interdigitation is already seen in ref. [10]. These links between the individual layers may be the reason for this long-range attractive force. In the surface force experiments force differences are measured by changing the plate separation with respect to the force at a certain plate separation. Thus the solvation force measured in the experiments depends strongly on at which plate separation the zero level of the force is taken. On the other hand, the force measurements are sensitive to the stiffness of the force-measuring spring and on the equilibration time used for each force measurement. These factors may explain why Granick *et al.* found oscillations in their solvation force around zero, while Israelachvili *et al.* only found a long-range attractive force.

In the simulations of Wang *et al.* no remarkable difference is found in the solvation force between linear octane and branched iso-octane. However, if we compare the results of the solvation force in more detail, we find that the maxima in our solvation force have a value of 266, 153, and 99 MPa, in comparison with much lower values (86.5, 32.6 and 13.7 MPa) in their results. This is caused by a much higher density of alkanes between the plates in our simulations. In the simulations of Wang *et al.* the molecules could flow in and out the slab and could evaporate and condensate in order to mimic a liquid droplet at the slit that is in equilibrium with its vapour. The resulting alkane density is, hence, 0.55–0.60 g/cm^3 in the slit, which is in the metastable region of the liquid-vapour coexistence.

In summary, we found a large difference in the solvation force for linear and branched alkanes. For n-decane, we found an oscillatory behaviour in the solvation force with periodicity close to the width of the molecule. For the branched molecules, we found that the oscillations are decreased and are shifted to the attractive region, which might be the result of more interdigitation.

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