HYDROPHOBIC INTERACTION BETWEEN A METHANE MOLECULE AND A PARAFFIN WALL IN LIQUID WATER ☆

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Monte Carlo simulations of the hydrophobic interaction between a spherical CH_4 molecule and a flat paraffin wall yield the surprising result that the water does not drive the methane molecule into contact with the wall, but rather favours a solvent-separated configuration in which the methane molecule is separated from the wall by one monolayer of water molecules.

1. Introduction

The hydrophobic properties of aqueous solutions of hydrocarbons [1–5] are a reflection of the unique properties of liquid water. Liquid water is a very structured fluid with strong hydrogen bonds. The ionic character of these bonds makes water a poor solvent for non-polar solutes like hydrocarbons. The insertion of a non-polar molecule perturbs the water structure in such a way as to minimize the loss of hydrogen bonds. For small non-polar solutes this is best accomplished by the formation of a clathrate structure around an isolated solute molecule. This leads to a reduction of the entropy of the neighboring water molecules. It was long thought that the water cage surrounding two non-polar solutes would order less waters when the two solutes are placed in contact than when they are separated far enough apart for them both to be completely surrounded by waters. This is because the interfacial area between the solute and the solvent will be smaller in the former case and the entropy decrease associated with the ordering of the water molecules will be relatively smaller. It follows from this that the free energy of the solution is expected to be lower for the solutes in contact than for solvent-separated pairs after the free energy of mixing is removed. This gives rise to the conventional view that there is a hydrophobic driving force towards contact or aggregation. Although there had been speculations to the contrary [2] the relative stability of a solvent-separated pair was first suggested by the semi-empirical integral equation theory of Pratt and Chandler [6]. Early simulations of Geiger et al. [7], though not calculating the potential of mean force, describe the hydrophobic hydration of a neon pair in contact and the solvent-separated pair, but does not give any prediction about the relative stability of these pairs. The first reliable molecular simulation to determine the potential of mean force between two non-polar spheres in ST2 water [8] was carried out by Pangali et al. [9,10]. Their simulations gave a potential of mean force with two minima corresponding to the spheres in contact and the spheres separated such that they occupied two clathrates with a common face between them. The radial distribution of one sphere relative to the other exhibits two maxima corresponding to these minima, but the volume element makes the second maximum larger; therebye forcing the conclusion that this solvent-separated configuration is more probable than the pair in contact. This conclusion has been corroborated by others [11–13].

In this paper we investigate how a non-polar sphere (like methane) distributes itself between two flat paraffin walls in water. This is equivalent to studying the hydrophobic driving force of a small hydrocarbon towards a large hydrophobic surface. Clearly the flat walls should perturb the water structure dramatically [14]. One can regard a wall as a spherical particle with an infinite radius of curvature. If one

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considers a small sphere near a large sphere it is difficult to anticipate the result. One cannot form two clathrates around the "large" sphere and the small sphere. One might argue that the free energy will be lower for the small sphere in contact with the large sphere than for the solvent-separated case. The simulations reported here are therefore very interesting because the solvent-separated free energy minimum is found to be much lower than the minimum corresponding to contact. Thus even here there is no strong driving force towards contact. If these simulations turn out to disagree with experiments it will be because several important things are left out of the potential models. These are discussed in section 4.

Systems of pure water between walls have been studied previously by a number of investigators using computer techniques [15–22]. The liquid–vapor interface has been studied [23,24] as well as the liquid–ice interface [25]. Dissolved ions [26,27] have also been studied, but no measurements of the solute potential of mean force relative to the walls have been done previously.

2. Methodology

We have used computer simulations of a small water system to study the hydrophobic effect on the molecular level. The system is specified by the interaction potentials between all the molecular species and the position of the walls relative to one another. The paraffin walls are the same as used by Lee et al. [14], i.e. two flat walls located at $2L$, where $L=11.81$ Å, from each other. The water–wall interaction was taken to be $V_{\mathrm{ww}}(z)=a_1/z^9-a_2/z^3$, where z denotes the distance between the wall and the oxygen of a water molecule. The parameters $a_1=4170$ kcal mole^{-1} Å^9 and $a_2=18.2$ kcal mole^{-1} Å^3 correspond to a water–paraffin interaction [14]. A methane–wall interaction potential was constructed from Lennard-Jones parameters [28] for a sheet of methane molecules interacting with another methane. This potential was parameterized for a single site methane molecule as $V_{\mathrm{mw}}(z)=b_1/z^{10}-b_2/z^4$ where $b_1=145171$ kcal mole^{-1} Å^{10} and $b_2=154.388$ kcal mole^{-1} Å^4. Thus a flat as opposed to a real, corrugated surface is used. For simplicity we treat the methane molecule as a sphere. It is a simple matter to simulate a more realistic methane–water interaction [29,30], but since we are interested in the general behaviour this refinement has been left out. Thus the methane–water interaction was modeled as a Lennard-Jones interaction with parameters fitted to give correct Henry's law behaviour [6]. Finally the water–water interactions were modeled by a refined water model allowing for internal vibrations, RWK2-M, developed by Watts and co-workers [31–33] which has been shown to yield good agreement with both thermodynamic and spectroscopic data. All interactions were spherically truncated at a distance of 8.2 Å and the temperature was set to 300 K. Thus with the exception of a change in water–water interactions we have elected to study the same *model* system as Lee et al. [14], i.e. with spherical truncation of the interactions at a distance much less than the extent of the entire system [#1].

The Metropolis Monte Carlo [34] algorithm was used to sample the 216 molecules in the system, augmented by preferential sampling [29,35,36] of the dissolved methane and solvent molecules around the solute. In order to avoid the sampling problems with only one solute, an umbrella sampling scheme was used [9,36,37]. This is equivalent to carrying out several simulations where the solute is confined by a harmonic potential to a small window along the normal of the wall and then piece together, from these snippets, a full wall–methane distribution. The additional constraint imposed by the restoring potential is corrected for in the sampling weights of each configuration. In the pure water system between the walls the initial ice configuration was equilibrated until all remnants of the initial structure was gone. Then the simulation was run for an additional 40K passes to ensure good statistics (one pass consists of a trial of each of the particles in the system). For the

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[#1] Recent simulations of Valleau and Gardner [21,22] reported problems in the convergence of simulations of a pure water system confined between two hard walls at room temperature. Although our system is different we encounter only minimal problems of this nature. We ascribe this difference to the problem of long range correlations imposed on these types of model systems when the range of molecular interactions are of the same size as the system investigated. Increasing the potential cutoffs in our system does indeed introduce similar correlations to Valleau and Gardner.

methane solvation 12 windows were used along the wall normal to calculate the distribution function, where each window was sampled for 10K passes. In this case a pass consists of N trial moves with the proviso that the solute and molecules around the solute have been preferentially sampled.

3. Results and discussion

3.1. Pure systems

In order to fully characterize the system we initially carried out a Monte Carlo simulation of the pure system without a solute. Long runs were performed from an initial ice-like structure to the fully converged, liquid-like, system. The build up of water density near the walls is best studied looking at the wall–oxygen correlation function along the wall normal. Fig. 1 shows both the true distribution and the symmetric distribution obtained by folding the true distribution along the midway point between the walls. The slight asymmetry is comparable to what Lee et al. [14] found for their system using the rigid ST2 water–water potential [8], and is an indication of the intrinsic error in the simulation. We have used the symmetrized system for the evaluation of all further quantities.

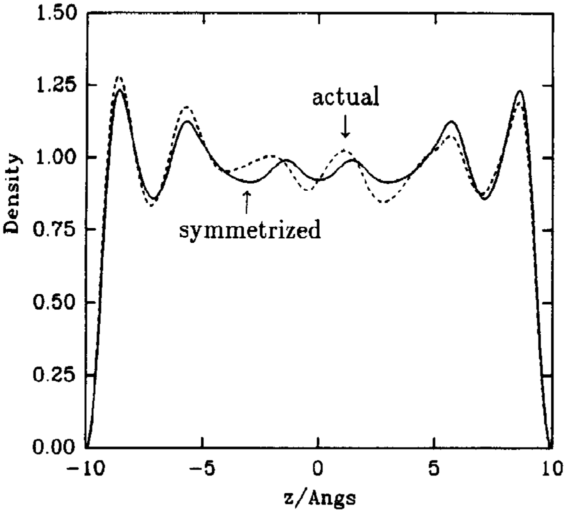

Fig. 1. The correlation function $g_{\text{wall-oxygen}}(z)$ relative to liquid densities. The wetting of the walls is seen as a buildup of oxygen density near the walls. Roughly six peaks can be seen in the figure corresponding to six water layers. At midpoint the liquid has obtained liquid densities and the influence of the walls is negligible for this system. The difference between the folded and non-folded distribution gives an indication of the error of the distribution function. The error bars are around 10%.

The system consists of six layers of water molecules between the walls with a liquid-like density in the middle region of the system. The first peak nearest to the wall is larger than the others but is smaller than the first peak in the oxygen–oxygen radial distribution of pure water. The wall breaks the underlying tetrahedral structure of the liquid, reducing the number of hydrogen bonds available to interfacial water. As the lost hydrogen bond on the average points into the wall an interfacial water is repulsed by the wall. This creates the additional buildup of water density near the surface seen in fig. 1. The strong hydrogen bond network makes water a very cohesive fluid. Lennard-Jones particles with parameters of the oxygen–oxygen interaction in ST2 water [8] are much less cohesive than liquid water and simulations of these entities in the same geometry show a strong build up of particles at the wall, in fact the liquid is depleted in the middle.

The angular distribution of the dipole and OH vector of the water molecule with respect to the inward wall normal is shown in fig. 2 for the interfacial region and the bulk. The interfacial region corresponds to the first solvent peak closest to the wall in fig. 1, and the bulk region correspond to the rest of the liquid. Further subdivision of the bulk yielded no additional information regarding the orientational behaviour. The bulk region shows a random orientation with respect to the wall normal for both the dipole and the OH vector as expected. The OH angular distribution at the interface has a maximum at the parallel orientation to the surface but pointing slightly into the liquid, two secondary peaks at the almost parallel or almost antiparallel orientation to the surface normal are also seen. The water dipole orientational distribution is broader than the OH distribution and tend to orient approximately parallel to the surface with a slight preference of pointing slightly outward from the liquid. This is an indication of a rather ordered interface where the first wall layer of the waters have reoriented themselves to develop a maximum number of hydrogen bonds with the bulk waters.

The structure of water near the paraffin wall is very

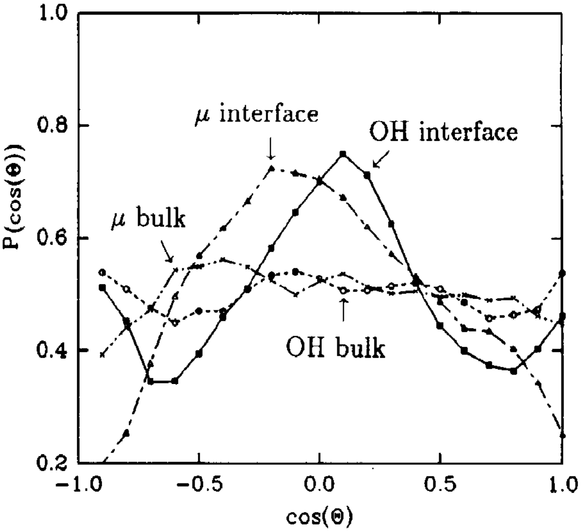

Fig. 2. The orientational correlation function of the internal OH bond and dipole of the water molecules with the normal of the paraffin walls for bulk and interface regions. A value of +1.0 corresponds to a given vector pointing into the fluid, 0.0 parallel, and −1.0 of a vector pointing into the wall. The interface region corresponds to the first peak of water density around the walls, bulk region includes all other water molecules in the system. The bulk orientation is random for both the dipole and the OH director. The interface regions show a tendency for the OH bonds to lay flat on the surface with a few bonds perpendicular to the surface. The dipole orientation is somewhat more pointing inwards than the OH distribution but with no dipoles pointing either straight in or our from the surface.

similar to that found by Lee et al. [14] even though the water–water potential is different. The almost flat interface can be constructed by using two idealized tetrahedral structures in which to orient the water and is consistent with the orientational distribution in fig. 1. In general there is an avoidance of water molecules having their OH bond, or their dipole vector pointing directly into the wall.

In ref. [14] the oxygen distribution using the ST2 model of water relative to the wall is similar to our results, with the difference that the RWK2-M water model used here has a slightly reduced first oxygen peak. The orientational ordering of the waters persist further into the fluid for the rigid ST2 model than the flexible RWK2-M water. This is a general reflection of the more ordered structure of the ST2 model of water in general.

Around a spherical non-polar solute in bulk water the surrounding waters can straddle the surface while maintaining the hydrogen bonded network characteristic of bulk water [7,10,38]. At a flat surface the waters need to reorient such that their OH bonds assume a more parallel orientation with respect to the wall in order to be able to maximize their hydrogen bonding with the fluid. This is of course consistent with the cage building that is permissible around a spherical solute as opposed to a large flat surface.

3.2. *Methane solvation*

A spherical particle representing methane was inserted into the water between the paraffin walls in order to study the distribution of the methane relative to the wall. The methane molecule was treated as a structureless Lennard-Jones particle interacting with only the oxygen atom of the water molecule. Allowing the solute to roam freely in solution would have caused severe problems in sampling all relevant wall distances. To prevent this, the specific umbrella sampling scheme employed by Pangali et al. [19] was used. Separate simulations were carried out for a set of overlapping harmonic windows along the wall normal, where the methane molecule was confined. The distribution was then reconstructed as spelled out in ref. [9].

The methane wall probability distribution, $P(z)$, is shown in fig. 3. For reference the gas-phase methane–wall distribution (obtained from $P(z)=A\,e^{-\beta[V(z)+V(L-z)]}$, where $V(z)$ is the methane–wall interaction potential, $\beta=1/kT$, and A is a normalization constant) is also shown. The two maxima displayed correspond respectively to the methane in contact with the wall (first peak from right) and the methane separated from the wall by a single water molecule. The solvent-separated configuration is clearly more probable. In this configuration one water molecule is situated between the wall and the methane. The water trapped between the methane and the wall has both of its OH bonds parallel to the wall, enabling it to engage in three hydrogen bonds with the closest waters constituing the cage around the methane. Any other water orientation would either have to point one of its hydrogens directly into the wall or into the methane, thus decreasing the number of hydrogen bonds available to that water. The first peak of the methane–wall distribution, the con-

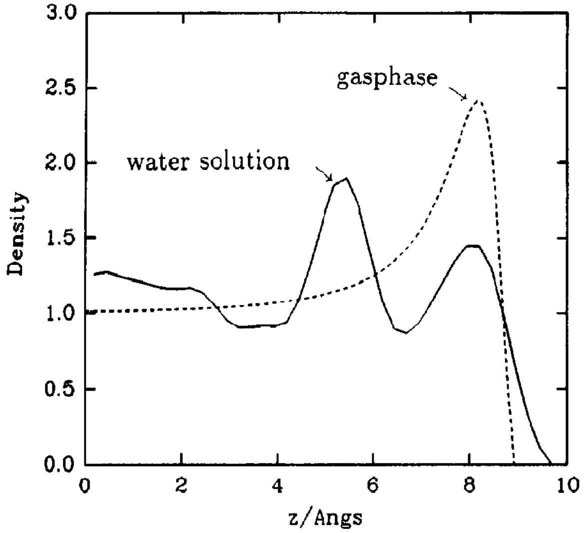

Fig. 3. The distribution function of methane molecules relative to the wall for the gas phase and the solvent phase. In the gas phase there is only one maximum corresponding to the wall contact separation, whereas in solution the methane behaviour is more complex. The appearance of the second, larger peak shows the solvent-separated configuration to be the preferred one. The second peak position is approximately one water diameter in from the surface. Graphs are drawn with equal area to facilitate comparison. The error can be estimate to be around 10% for the solvent phase graph.

tact separation, has been pushed towards the wall relative to the gas phase.

The stability of the solvent-separated configuration is similar to what was found previously for a system of two inert solutes in bulk water [9,10,12,13]. There it was shown that the water cage surrounding the two solutes was most stable with two interconnecting cages placing a water molecule between the solutes [7,10,38].

The potential of mean force $W(z)$ is defined as the reversible work required to bring the methane molecule from infinite separation to a distance z away from the wall. This corresponds to the Helmholtz free energy. Given the probability distribution $P(z)$ in fig. 3 $W(z)$ is determined up to a constant shift in energy by

$$W(z) = -\beta^{-1} \ln P(z) + C . \tag{1}$$

In order to isolate the *solvent* contribution to the hydrophobic effect we can remove the effect of the wall by subtracting off the methane–wall potential,

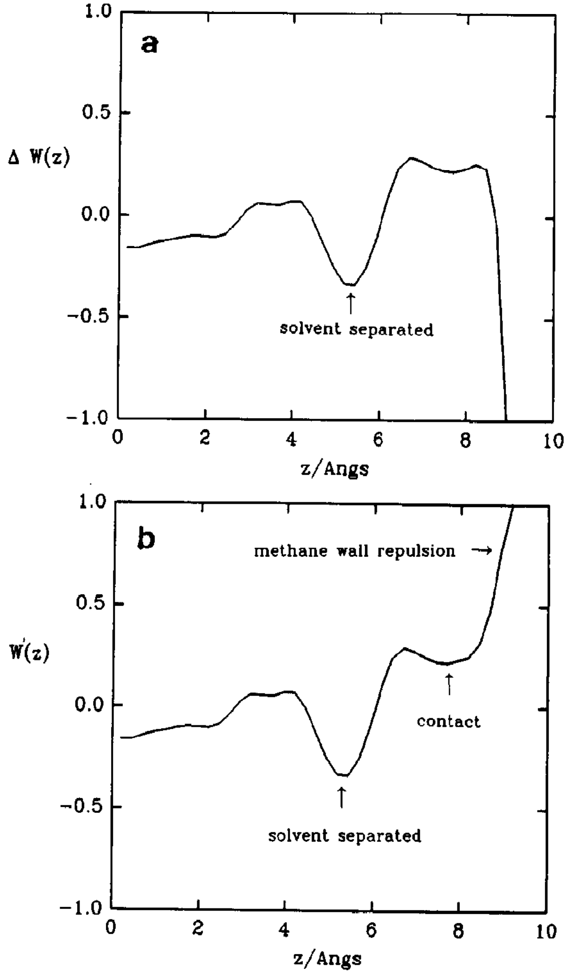

Fig. 4. (a) The potential of mean force in units of kcal mol^{-1} for the condensed phase where the contributions from the methane–wall interactions have been removed. There is no large minimum corresponding to the first peak in fig. 3, indicating that the wall contact separation is mainly due to the methane–wall interaction. The solvent-induced minimum is clearly seen. The picture corroborates the conclusion of the more stable solvent-separated minimum for the non-polar molecule when immersed in a water like solvent. The sharp dropoff at 9 Å reflects the fact that in the absence of the walls the methane would like to float on top of the water layer. (b) The potential of mean force in units of kcal mole^{-1} for the system where the methane–wall interaction is purely repulsive. Here the wall contact minima is seen to be very shallow and unstable relative to the much deeper solvent-separated configuration.

$V_{mw}(z)$, from the potential of mean force,

$$\Delta W(z) = W(z) - [V_{mw}(z) + V_{mw}(L-z)] . \tag{2}$$

In fig. 4a $\Delta W(z)$ is shown. As there is now only one strong relative minimum within the range of fluid we see that the first peak in fig. 3 was mainly due to the attractions of the methane–wall potential. There is now a new weak local minimum corresponding to contact between methane and the wall. The deep minimum at the wall results from the fact that in the absence of a wall–methane potential the methane would like to float on the surface of the water. If the methane–wall interaction is taken to be a purely repulsive potential corresponding to the CWA [39,40] truncation of $V_{\mathrm{mw}}(r)$, the potential of mean force will be given by

$$W'(z) = \Delta W(z) + V_{\mathrm{mw}}^{\mathrm{WCA}}(z) \; . \tag{3}$$

This is shown in fig. 4b. Here we clearly see that there is a very shallow minimum representing the contact between the sphere and wall, and a much deeper minimum representing a solvent-separated configuration where the sphere is separated from the wall by one water molecule.

The hydration cage of the methane is stabilizing the configuration in which the methane molecule is located one hydration shell away from the wall. The water molecule separating the methane from the wall is essentially oriented with its OH bonds parallel to the surface. This enables the water molecule to maximize the number of hydrogen bonds it can engage in. The avoidance of the wall contact state is a property of the water since in the gas phase the solute is preferentially located at the wall. Thus the ability of the solvent to accommodate the solute molecule *and* remain hydrogen bonded determines that the solute will be solvent separated from the wall.

4. Conclusions

Neat liquid water between two flat parallel paraffin walls slightly wets the walls. As expected the effect of the walls is most noticeable in the first solvation layer; and the water molecules midway between the walls behave as in bulk water. The majority of water molecules in the first layer are oriented with the OH bonds of the water molecules pointing parallel to the wall. This maximizes the number of hydrogen bonds.

We have shown that a hydrophobic solute is not forced into contact with the wall by the water. The ability of the interfacial water molecules to retain their hydrogen-bonded network stabilizes a solvent-separated configuration, and gives rise to a global minimum in the potential of mean force.

It would be desirable to determine how sensitive the solvent-separated configuration is to changes in the interaction potentials. In particular the cooperative nature of water solvation has not been fully investigated [41–43]. Most liquid water properties can be reproduced by effective two-body potentials [44], but these models do not simultaneously reproduce properties of water clusters and bulk water. Thus a water model with a charge distribution constructed to yield an effective liquid dipole moment will invariably give too high a dipole moment for a monomer or a cluster. Interfacial properties should be especially sensitive to these problems as the electrostatic character of interfacial water should be somewhere between that of a monomer and that of a liquid state molecule. A correct treatment of the electrostatics of water would include self-consistent many-body polarization forces [41], which could change the water structure at the walls from what is found here. The change might weaken the hydrogen-bonded network near the wall, as the dipoles of the interfacial water would be smaller than in bulk water. This could have an effect of increasing the solvent driving force on a methane molecule towards the wall.

It is worth commenting that a real surface is bumpy. It is possible that the hydrogen-bonded network is sufficiently perturbed near a realistic bumpy surface and that there will be a greater driving force toward contact with the wall. This remains to be seen.

As matters now stand the picture that emerges from consideration of water models with two-body interactions, is that there is a hydrophobic driving force pushing non-polar spheres towards a solvent-separated free energy minimum with the wall and not towards contact as more primitive theories would have it. This picture may change when more realistic many-body potentials are adapted.

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